PART II.

THE TECHNOLOGY OF PETROLEUM.

PART II.

CHAPTER I.—MIXTURES OF PETROLEUM.

SECTION 1.—FILTERED PETROLEUM.

Petroleum was prepared for use, particularly in medicine, by filtering, at a very early date in southern Ohio Dr. Hildreth, as early as 1833, (*a*) mentions filtering petroleum through charcoal, by which much of its "empyreumatic smell is destroyed and the oil greatly improved in quality and appearance". Since that time petroleum has been filtered through gravel and through both wood and animal charcoal, in order to remove all sediment from it, and at the same time to remove in part both its color and its odor; but since the methods of refining by distillation have been discovered, it is chiefly the more dense oils that have been treated in this way. These dense natural oils are often injured by distillation in the properties which render them valuable for lubrication, and filtering appears to furnish the only means of removing, even in a partial manner, the color and the often quite disagreeable odor.

SECTION 2.—MIXTURES OF PETROLEUM.

The mixtures into which petroleum enters are chiefly used for lubrication. They consist of petroleum and heavy products of petroleum mixed mechanically with animal and vegetable oils, tallow, resin, and allied materials, of the same mixed with mineral substances, and also of the same mixed with chemical compounds. The first class of compounds is made in very great variety; in fact, there is scarcely a wholesale oil house in the country but has some formula of its own for compounding lubricating oils, into which petroleum or the products of petroleum enter as a constituent. Some of these are sold honestly as mixtures, while others are adulterations pure and simple. Some of these mixtures are prepared in the rudest manner, and are used only for the coarsest purposes; others are prepared with great care, the mixture being effected by heating and purified by straining or filtering the oil through various materials. The general purpose for which mixtures are prepared is to produce a lubricating material that will be quite as effective as animal or vegetable oils and at the same time be less expensive. A few mixtures are prepared and sold on their merits as preparations of a superior quality, while some dealers maintain that the larger the proportion of mineral oil the better.

The oils used in preparing these mixtures are sperm, whale, and lard oils to a considerable extent, especially for lubrication. Neat's-foot oil and castor oil are used in mixtures for dressing leather. Lard-oil mixtures have been used for oiling wool. In Germany a mixture is sold under the name of "Vulcan oil", which consists of a petroleum distillate of a specific gravity of from 0.870 to 0.890, treated with about 6 per cent. of sulphuric acid and well washed with water, and then mixed with 5 per cent. of rape oil. Another, called "opal" oil, consists of petroleum distillate of a specific gravity of from 0.850 to 0.870, similarly treated and washed, and mixed with 10 per cent. of rape oil.

The mixture of petroleum products with mineral substances have only been invented quite recently, and are principally the so-called plumbago oils manufactured in Rochester, New York. By a process which has been patented, reduced petroleum is apparently ground with graphite, as paints are ground in oil, resulting in a complete suspension of the graphite in the oil. It is claimed that these oils are very superior lubricators for railroad axles and steam cylinders, the latter becoming coated with a polished coat of graphite soft as silk. The Johnson Graphite Oil Company publishes a certificate showing that a car had made over 13,000 miles of mileage on one application. It has also been proposed to treat heavy reduced oils with powdered pyrophyllite. This mineral resembles talc, and when powdered is especially soft and greasy to the touch.

The most striking example of chemical preparations of petroleum is perhaps found in the justly celebrated Galena oils, manufactured at Franklin, Pennsylvania. These oils consist of a lead soap dissolved in petroleum. A lead soap is prepared after the ordinary manner by boiling oxide of lead with a saponifiable oil, and the whole is dissolved in the natural heavy oil of the Franklin district. The oils thus prepared have great tenacity and endurance as lubricators, particularly for car-axles, for which purpose they are principally used.

Mixtures of natural oils and tallow, natural oils and residuum, reduced petroleum, residuum from acid-restoring works, containing sulphur, pine tar, etc., are used on car-axles and for other heavy lubrication.

a A. J. S. (1), xxiv, 63.

CHAPTER II.—PARTIAL DISTILLATION.

SECTION 1.—SUNNED OILS.

The thickening by evaporation of oils spilled upon the Allegheny river and its tributaries, by which an ordinary third-sand oil would become converted into a dense oil fit for lubrication, led to experiments upon the lighter first- and second-sand oils around Franklin that were too light for lubricators and too dense for profitable manufacture into illuminating oils. These experiments were first undertaken by Mr. William H. Brige, of Franklin, and consisted in an attempt to imitate the conditions observed on the river as nearly as possible. Mr. Brige first exposed the oil spread on the surface of water in a small pan 3 feet square. This pan was placed in the sun, and the light oils were allowed to evaporate until the desired consistence was reached. The method was found to be entirely successful. The plan, since adopted on a larger scale, is as follows: A wooden tank is provided, sunk in the ground nearly its entire depth, 60 to 70 feet long, 20 to 30 feet wide, and 1 foot deep. A flat steam coil is laid upon the bottom, and water is run in from 8 to 10 inches deep, upon which a layer of oil about an inch thick is placed. The water is heated by the coil to about 110° F., and the oil becomes very limpid. Every description of dirt, particularly minute particles of grit, that was held in suspension in the viscid oil is left free to fall to the bottom of the tank, and the specific gravity of the oil is reduced in a few days from 32° to 29° B. The oil loses by this treatment about 12 per cent. of its volume, and is increased in value from $5 to $12 per barrel.

SECTION 2.—REDUCED OILS.

Throughout the entire region the observation has been made repeatedly that oil left in open tanks evaporates and decreases in specific gravity Baumé. Mr. George Allen, of Franklin, acting on such observations, patented a novel method of partially evaporating petroleum which produces a very superior quality of oil. He suspends sheets of loosely woven cloth vertically above troughs in a heated chamber and by a perforated pipe distributes the oil upon the upper border of the curtain in thin streams. The oil is thus distributed over a large surface in the heated atmosphere, and the thin film is rapidly evaporated, the light portion passing into the atmosphere, and the heavy portion dripping from the lower border of the curtain into the troughs, from which it passes into a receptacle. This method of treatment furnishes a bright green, odorless oil, entirely free from sediment of any kind, such impurities remaining attached to the curtain. These methods of partial evaporation are particularly valuable, as they preserve all the qualities of the natural oil, without any danger from the effects of overheating.

Many thousands of barrels are reduced every year by partial evaporation in stills, either by direct application of heat or by the use of steam, the evaporation for this purpose being always so carefully conducted as to avoid overheating and "cracking" or any approach to destructive distillation. The different grades of naphtha are usually run off, and then a sufficient amount of distillate is removed to reduce the portion remaining in the still to the required specific gravity. The amount of reduction depends upon the purpose for which the oil is intended, not only with regard to its density, but also with regard to the velocity and temperature at which the machinery is to be run. For use on large journals and those revolving at moderate speed the oil is reduced to a specific gravity of from 29° to 32½° B., but for use on small journals moving with great velocity, and also in the interior of cylinders, where the temperature is very high, a still greater reduction is found necessary, and the oil is made more dense. At the same time it is made less volatile, having a specific gravity of from 26° to 29° B.

A large proportion of the lighter grade oils of West Virginia and Ohio and the entire production of the Smith's Ferry district are treated in this manner. The latter oil is very peculiar, having the color of pale sherry, without its transparency, and when freshly pumped has a specific gravity of 50° B., with a much less pronounced and less disagreeable odor than any other petroleum produced in commercial quantities in the United States. When reduced with the aid of steam the distillate of suitable specific gravity for burning oil requires little or no treatment with acid or alkali, and the reduced oil from the still preserves its amber color and freedom from offensive odor, furnishing a lubricator of very superior quality and attractive appearance.

Reduced oils are often filtered through animal charcoal, and are thereby greatly improved in color and odor.

Chapter III.—GENERAL TECHNOLOGY OF PETROLEUM BY DISTILLATION.

Section 1.—INTRODUCTION.

Oils were first obtained for commercial purposes by distilling shales and coal early in the present century, but they had been thus produced in small quantities for experiment more than a century before. Gesner, in *Coal, Petroleum, and Other Distilled Oils*, 1861, page 8, says:

As early as 1694 Eele, Hancock, and Portlock made "pitch, tar, and oyle out of a kind of stone", and obtained patents therefor. * * * In 1781 the earl of Dundonald obtained oils from coals by submitting them to dry distillation in coke ovens. * * * Laurent, Reichenbach and others distilled the tars obtained from bituminous schists. These tars were purified in some degree by Selligne, and the oils subsequently obtained an extensive sale in Europe for burning in lamps and for lubricating machinery. * * * Patents were granted in England in 1847 to Charles Mansfield for "an improvement in the manufacture and purification of spirituous substances and oils applicable to the purposes of artificial light", etc. Mr. Mansfield's operations appear to have been chiefly directed to the coal tar of gas works, from which he obtained benzole. He was perhaps the first to introduce the benzole or atmospheric light, which is described at length in his specifications.

From a letter received from the eminent English geologist, E. W. Binney, I extract the following statement concerning the origin of the paraffine oil industry of Scotland:

In 1847 Mr. James Young came to me to ask for information as to petroleum, he having agreed to work some at Riddings, near Alfreton. I gave him all the information I possessed. In 1848 I went over with him to Down Holland Moss(*a*) and showed him the petroleum peat there and brought away samples for him. In the same year I went to Riddings and descended Mr. Oakes' coal-pit and examined the petroleum as it came from the roof of the coal-seam. I then distinctly told him that the oil could be made from highly bituminous coal, distilled at a low heat in a something similar way as the peat and gas-coal yielded it. In 1850 Mr. Young and I became aware of the discovery of a highly bituminous coal at Boghead, in Scotland. We met at the British association, in Edinburgh, at the end of July. I went over to Bathgate, descended the pit where it was wrought, brought a sample of it, and showed it to Messrs. Young and Meldrum, who said they thought it would not make oil. I said that if they could not make oil from it I could. In a day afterward they asked me to join them in a patent to work the invention. Mr. Young was to take out the patent in his name, and Mr. Meldrum and I were to join him in owning and working it. I accordingly bought land, found money, and purchased 10,000 tons of Boghead coal. These works were carried on under the style or firm of E. W. Binney & Co. for fifteen years. I drew the specification of the Young's patent and invented the name paraffine oil, which term was quite new. In 1856 I took out an American patent in Mr. Young's name for the invention, and several parties took licenses in the United States to work it there, paying 2 pence per gallon royalty to us, they fetching Boghead coal from Scotland at a cost of £4 or £5 per ton when delivered. Breckenridge and some other American coals were also used, I believe. As some of these parties refused to pay their royalties, we went to law with them in the states, and their lawyers, having heard that our patent had been the subject of a trial in the court of Queen's Bench, wrote to England for the history of Young's patent, which was reported in the *Journal of Gas Lighting*, in a trial at law, Young *vs.* Hydrocarbon Gas Company, June, 1854. In this trial Mr. Young gave in evidence that he obtained paraffine oil from petroleum before he resorted to coal to obtain it. That would be about 1860; and our American patent never yielded us another cent of royalty. Oil lamps for burning it having been invented in Europe, all was ready for the start of your vast petroleum trade. We always dreaded your native oil coming on us, but we did pretty well before it rushed out, and our patent expired in 1864.

There was no lack of information in this country respecting the properties of petroleum prior to 1860.

Professor Silliman, sr., in 1833, wrote:

I have frequently distilled it in a glass retort, and the naphtha which collects in the receiver is of a light straw color and much lighter and more inflammable than petroleum. On the first distillation a little water rests in the receiver at the bottom of the naphtha, from which it is easily decanted, and a second distillation prepares it perfectly for preserving potassium and sodium, the object which has led me to distill it. (*b*)

In a communication made to the Bradford *Era* of July 4, 1881, some one signing himself "Old Salt Well" gives the following story of the first attempt to refine petroleum in northwestern Pennsylvania. Speaking of the salt-wells near Tarentum, Armstrong county, Pennsylvania, which, with the springs on Oil creek, at that time produced all of the petroleum of that region, he says:

To my certain knowledge they only produced from three to five barrels per day, and I recollect distinctly there was but one well that produced oil only. The wells were pumped, the oil mingling with the salt water. The wells were owned by a gentleman named Kier. When the wells first yielded oil it was placed in four-ounce vials and hawked about the country at 25 cents per bottle as Seneca or rock oil for medicinal purposes. In the year 1854 a small refinery was built at the corner of Grant street and Seventh avenue, Pittsburgh, the point of the old canal outlet into the Monongahela river and the same locality of the present railroad tunnel. It was there the first carbon oil was refined for illuminating purposes. The still did not have a capacity exceeding five barrels. It occupied a one-story building, in size about 12 by 24 feet. In the spring of 1855 I purchased a gallon of the oil, had it placed in a stone jug, and took it home for the purpose of illumination. The kind of lamp in which the oil was used was the same as what was then employed for a substance called burning fluid. The lamp had from one to five small tubes, and was made of britannia or pewter. To trim the lamps cotton-wick was drawn into the tubes, perfectly tight, and the wick was cut down closely until it ceased smoking, and then the lamp was nearly as perfect as any lamp of the period. Each one of those tubes produced a light equal to about two tallow candles. In the year 1876 or 1877 the still that was employed in this immense refinery was displayed at the exposition in Allegheny city, and was labeled as the first still ever used to refine petroleum. In its day it supplied the world's demand for that kind of an illumination. The matter of where the first oil was produced I believe is not the question. Any of the old salt manufacturers about Tarentum can corroborate

a On the coast north of the Mersey.

b A. J. S. (1), xxiii, 101.

what is here stated, and perhaps furnish many interesting details not contained in this brief article. These wells were located 18 miles from Pittsburgh, near the path of the old Pennsylvania canal. Colonel Drake was not the first man to produce petroleum, but he was certainly the first person who drilled a well for the express purpose of finding oil. The questions of when and by whom the first oil was produced and refined can readily be established by indisputable proof.

The Mr. Kier mentioned above was Mr. Samuel M. Kier, before mentioned in this report (see page 10), who, with his friend Mr. McKuen, carried on the enterprise as described. This statement is corroborated by a large amount of evidence from independent sources. It was not a lack of knowledge, but a lack of petroleum, that prevented its use by American manufacturers before 1860. Drake sold his oil to McKuen for 75 cents a gallon.

The editor of the *American Journal of Science and Arts* in 1861 reviewed Gesner's *Coal, Petroleum, and other Distilled Oils*, and says:

The author recognizes the intimate relation of the manufacture of coal oils with the production in such increasing abundance of petroleum, destined to become a powerful competitor of the artificial product for economic use. It is instructive in this connection to recall the fact that the natural product (petroleum), which has been well known from the earliest records of human history, should have remained comparatively useless and almost neglected until the modern art of coal-oil distillation has shown its industrial value. *It is quite possible that the future historian of the industrial arts may look back on the coal-oil distillation as only an episode in the history of the development of the use of petroleum.* (a)

In 1862 Isaiah Warren and his father, being in the lard-oil and candle trade in Wheeling, West Virginia, commenced the distillation of West Virginia petroleum in three 15-barrel stills, and Mr. Warren, sr., was apprehensive that they would glut the market, the price of refined oil then ruling at from 85 cents to $1 15 per gallon.

SECTION 2.—EARLY METHODS.

The stills in general use at this time were made in three parts, bolted or riveted together, and consisted of a cylindrical cast-iron body, to which was attached a boiler-plate bottom and a cast-iron dome and goose-neck. They held about 25 barrels, were heated from the bottom and bricked up upon the sides, and were sometimes protected from the direct action of the fire by fire-brick. These stills were charged with crude oil, the charge run off, the still cooled, and the coke cut out, often with a cold-chisel. When four-fifths of the oil had been run off the remainder was, when cold, as thick as pitch; at this point some refiners introduced steam, which mechanically expanded and carried over the last volatile portions of the charge, leaving a compact coke, while others distilled to coke without steam. The use of steam at a high pressure in the distillation of Rangoon petroleum and coal had been patented in England in 1857 by Mr. Bancroft, of Liverpool; and Mr. Wilson, a manufacturer of stearic acid, in 1860 used superheated steam in the distillation of natural petroleums. (b) Steam under moderate pressure was also frequently used throughout the entire distillation, both above the charge and injected through it. In the latter case it becomes superheated as the boiling point of the oils rises above that of water; it was, however, considered preferable with the dense paraffine oils to superheat the steam before it entered the oil. Sometimes, after the charge in the retort was partly run off, it was the practice to allow a stream of fresh oil to enter the still about as fast as the vapors were condensed. In this way about twice the ordinary charge could be distilled and the residue of the whole run down to coke. The light naphthas were first taken off and were used for fuel or were allowed to run to waste, there being at that time little or no sale for these products. The distillate was then run to illuminating oil until the specific gravity reached 36° B. = 0.843, and the remaining charge run down till the distillate became of a greenish color. The illuminating oil was then placed in an iron- or lead-lined tank and agitated for one or two hours with oil of vitriol washed, then with water, and afterward treated in the same manner with caustic soda solution of a specific gravity of 1.400 and again washed with water. Some refiners considered this successive treatment with acid and alkali sufficient; others subjected the treated oil to a second distillation, sometimes over solid caustic soda; but this distillation had to be conducted with great care. Some of the earliest and most successful refiners of petroleum on the Atlantic coast were formerly manufacturers of whale and sperm oil, and, having been accustomed to expose their animal oils to sunlight under glass roofs in shallow tanks, they adopted with uniform success the same method of treatment for the mineral oils. Both the color and the odor are improved by this exposure. The heavier naphthas and heavy oils were subjected to redistillation, either alone or with more crude petroleum, and all of the distillate of a proper specific gravity for illuminating oil was carefully separated. The remaining heavy distillate was treated with acid and alkali and sold as "paraffine oil". It was of a dark color and rank odor, and found its way into use very slowly, not only on account of its real inferiority, but on account of violent prejudice against it.

SECTION 3.—DESTRUCTIVE DISTILLATION.

The general method of manipulation just given was in very general use until about 1865, when the method of cracking or destructive distillation of the heavier oils was generally adopted. A great variety of chemical reagents were used in treating the oils. Solid caustic soda was used in the stills. The oils were washed with nitric acid; bichromate of potash was added to the sulphuric acid, and the combined action of sulphuric and chromic acids

a A. J. S., 1861.

b J. F. I., lxix, 338, 1860; Cosmos, Mar., 1860.

was thus secured; and chloride of lime or bleaching powder in the proportion of 3 ounces to one gallon of oil has been used with hydrochloric acid, the oil finally being treated with lime water. Whatever reagents are used in treatment, it has been found necessary to bring the oil to a uniform temperature above 60° F. In the old form of agitator, when the mixture was effected by machinery, the injection of steam during agitation has been found beneficial both for bringing the oil to the required temperature and to facilitate the washing and settling of the acid and alkaline solutions. (*a*)

In December, 1865, James Young, jr., of Limefield, took out a patent in England for an improvement in treating hydrocarbon oils that was noticed as follows in the *Chemical News* for August 31, 1866:

This looks like a very valuable invention. The patentee submits the heavier hydrocarbon oils to distillation under pressure, and finds that thereby the heavier oils originally operated upon are converted into oils of lower specific gravity, possessing a higher commercial value. The process may be carried on in ordinary steam boilers (not tubular), which should be proved to 100 pounds; but it is not found necessary to operate much beyond a pressure of 20 pounds to the inch. The means of regulating the escape of the vapor, and of condensing it, can be easily imagined. The operation may be carried on with the crude products of the original distillation, or the lighter oils may first be separated by an ordinary rectification, and only the heavy oils submitted to this treatment. (*b*)

At about the time that this invention was patented in England the same results were obtained in the United States by an entirely different method of manipulation. This method consisted in a slow and repeated distillation, which produced destructive distillation of the medium and heavy oils, converting them into oils of a density suitable for illumination with a production of gaseous products and deposition of carbon. In order to accomplish this result the brick casing was removed from the stills, and after that portion of the distillate suitable for illumination had been separated the fires were slackened and the vapors of the heavy oils as they rose into the dome of the still were allowed to condense and drip back upon the hot oil below, which had meanwhile been heated to a temperature above the boiling point of the oil dripping upon it. This practically superheats the vapors of the oils and produces decomposition. The effect of distillation under pressure is precisely the same: the oils are distilled at a temperature above their normal boiling points. By this method of distillation the petroleum can be converted into naphtha, illuminating oil, and coke, with a certain amount of gas either escaping into the atmosphere or being burned as it escapes. The illuminating oil may be collected in one receptacle and be made of uniform grade, or that portion of the petroleum suitable for purposes of illumination can be separated from that produced by destructive distillation, thus furnishing two grades of illuminating oil which are quite different in composition and quality, the light oils in the crude petroleum being superior to those produced by the decomposition of the heavier portions of the oil. This method of distillation had been successfully pursued in treating the distillates from coal before the introduction of petroleum, but it was not generally applied to the treatment of petroleum, especially in very large stills, until about the time here indicated. Its successful introduction and general adoption was, however, the result of an accumulated experience, not only in the distillation, but quite as much in the subsequent treatment of the oil with acids and alkalies, especial regard being had to the temperature while undergoing treatment. The result of the adoption of this method of manipulating the oil by one distillation was the gradual separation of petroleum refiners, in a general way, into two classes: a small number who continued to manufacture a variety of products from petroleum, and a large number who manufactured principally illuminating oils. While the division thus made is correct in a general sense, it must not be understood as applying strictly to all the parties engaged in manufacturing petroleum. There are those who reduce petroleum and sell their light distillates; others who reduce petroleum and treat their own distillates; others who produce nothing but enormous quantities of crude naphthas, illuminating oils, and residuum, selling their crude naphtha to parties who redistill and fractionate the naphtha into several products—their illuminating oils to the general trade, and their residuum to manufacturers of lubricating oils; others who refine and fractionate crude naphtha; others who manufacture lubricating oils, using both crude petroleum and residuum for the purpose; others who manufacture in one establishment nearly everything that can be made from petroleum; and still others who have special processes by which peculiar products are obtained. It is unnecessary to describe in detail all of these different methods of conducting the business of manufacturing petroleum; it is sufficient for my purpose to describe carefully what may be termed two typical establishments, and then to describe a number of processes that are used for special purposes.

SECTION 4.—DESCRIPTION OF THE APPARATUS USED IN MANUFACTURING PETROLEUM.

Before describing the process above mentioned, it will be necessary to describe in detail the apparatus which is in general use in such establishments.

LOCATION.—The largest petroleum refineries in the country are at tide-water at Hunter's Point and Newtown creek, Long Island; Bayonne, New Jersey; Point Breeze, below Philadelphia, and at Thurlow, below Chester, on the Delaware; and near Baltimore, Maryland. At Bayonne, New Jersey, the Standard and Ocean refineries have piers 1,000 feet in length, with sufficient water to float the largest ships and facilities for loading from 6,000 to 7,000 barrels of refined oil daily. In western Pennsylvania and Ohio the refineries are usually located upon the side of a hill, the storage-tanks for crude oil being placed highest and the oil distributed by gravity so far as is possible.

a See *Chemical News*, vi, 230.

b C. N., xiv, 108.

BUILDINGS.—The buildings of refineries are in the greatest variety possible. In the older establishments, particularly in the Atlantic cities, the works are carefully inclosed with substantial buildings of brick and iron, while the other extreme is to be observed in newer establishments, either just going into operation or being rebuilt after destructive fires, when scarcely anything about the place except boilers, engine, and pumps is covered, the receiving-tanks being underground and the stills without any covering at all. The works of the Downer Kerosene Oil Company, at South Boston, have always been very carefully inclosed in valuable brick buildings, and no serious loss has occurred there for many years. Some of the immense refineries at and around Hunter's Point, Long Island, are also fully inclosed; but the works of the Tide-Water Pipe Company at Thurlow, Pennsylvania, on the Delaware, only recently constructed, and said to be one of the most complete establishments of the kind, are almost as completely exposed to the elements as those of the smallest and rudest concerns in the oil regions. The boilers are placed in one building, the pumps in another, the office in another, all of which are of brick; but the stills and condensers are without any covering whatever. The distillate tanks are all underground; the agitating tank is isolated and uncovered; and the sunning and spraying tanks are in buildings made of rough boards, and are of little value. The works of the Acme Oil Company, at Titusville, Pennsylvania, built to replace those burned during the census year, appear to be built on a hillside from which fire has removed even the soil, and to be without a building or a covering of any description.

TANKAGE.—The oil is received at the refineries either from pipe-lines or from the tank-cars of transportation companies, and in either case it is pumped into vast storage-tanks holding from 10,000 to 36,000 barrels each. The tank-cars are provided with gates or valves on the under side, to which hose may be attached, and connections are made with a large pipe laid beneath the track, into which the oil rushes as soon as the gates are opened. This pipe discharges the oil into a tank, from which it is pumped to the storage-tanks. In these tanks from one to two per cent. of water settles, and from them the oil is pumped into the stills.

STILLS.—A great variety of stills are in use for different purposes, and the greater the variety of products produced from the petroleum the greater will be the variety of stills in use as regards both size and form. In some establishments the old cast-iron, upright cylindrical still, with wrought-iron bottom, is still in use. To these have been added plain, horizontal wrought-iron cylinders of various sizes. One of these, as now quite generally used, is represented with the setting in the vertical section in Fig. 37, and a bank of three, as they are usually set, in Fig. 38. From these sections it will be observed that they are 12 feet 6 inches in diameter and 30 feet in length. The vapors rise into a dome 3 feet in diameter, from which they pass to the condenser through a single pipe 15 inches in diameter. No more simple form of still could be devised. The so-called cheese-box still, now in great repute, is shown with the setting in horizontal and vertical section in Figs. 39 and 40. It is 30 feet in diameter and 9 feet high, with a dome-shaped top, and works 1,200 barrels of crude oil. The bottom has a double curve, to allow of expansion; the sides are of five-sixteenths-inch wrought-iron and the bottom of five-sixteenths-inch steel, the whole inclosed in a sheet-iron jacket. The center is supported upon a cylindrical pier of brickwork, through which the products of combustion are led to the stack. The circumference is supported upon seventeen arches, in sixteen of which are fireplaces, the sides of which converge toward the center and discharge over a bridge-wall through four arches into the center of the pier just mentioned. Through the seventeenth arch passes the discharge-pipe from the bottom of the still. The vapors escape from this still through three pipes, two of which may be closed by cocks, into a sort of chest or drum (Fig. 41), from which 40 pipes 3 inches in diameter pass through to the condensing tanks. Steam is introduced into the heated vapors as they escape from both the cylindrical and cheese-box stills by placing a curved and perforated pipe of the form shown in Fig. 42 at the point where the vapors emerge from the still and enter the exit pipe. The use of steam in this manner is found to improve both the color and the odor, especially of "cracked oils".

Several attempts have been made to produce continuous distillation; but I cannot learn that any of them have proved commercially successful, although an apparatus of the kind erected in Buffalo has been put in operation and distillates have been produced that were treated and sold. This apparatus was patented by Samuel Van Syckle, of Titusville, Pennsylvania, May 22, 1877, No. 191203. It consists of a series of stills, in which the oil is maintained at a constant level by means of a tank, in which a float on the surface of the oil as it rises and falls automatically controls the flow. The first still is maintained at such a temperature that the naphthas and other light products are removed, and in the other two the illuminating oils are removed so effectually that residuum may be drawn off from the last still. I think this apparatus should be more thoroughly tested before its merits are finally judged, especially as to how far its value is modified by complexity and expense of manipulation.

Another apparatus, evidently much more simple in construction than Van Syckle's, but at the same time not calculated for handling the enormous quantities of oil refined in this country, has been patented in Germany by Herr Fuhst. (*a*)

The deodorized lubricating oils, of which Mr. Joshua Merrill, of the Downer Kerosene Oil Company, was the inventor, have been prepared by him in a still of peculiar construction, especially adapted to the treatment of petroleum and kindred substances. An accident suggested the preparation of these oils to Mr. Merrill. In

a Dingler, ccvii, 293.

November, 1867, the condenser to a still, in which a quantity of oil too heavy for illumination and too light for lubrication was being fractionated, became obstructed from some accidental cause, and the pressure became so great that the leakage caused the fires to be drawn and the whole thing to cool down. The still was started with 900 gallons, from which 250 gallons was found to be removed by the partial distillation. On removing the remaining oil, Mr. Merrill was surprised to find it different from any petroleum product he had ever seen before. "It had a bright yellow color, was clear, very nearly odorless, neutral, and dense. Further experiment showed this result to have been obtained by the removal of all the light odorous hydrocarbons without decomposing either the distillate or the oils remaining in the still; and that this had been accomplished by the moderate fire employed, and its gradual withdrawal." (*a*)

This mode of operating was immediately applied to other distillations, and in order to accomplish the result most effectually Mr. Merrill invented a method of superheating steam within the body of the oil itself. Within a still of moderate size, holding perhaps 1,000 gallons, he placed a steam coil, which terminated upon the exterior of the dome of the still. After attaching a valve, the steam-pipe is returned into the still and a perforated coil of pipe connected with it, which lies flat upon the bottom. The still is heated by direct heat, and as the temperature rises the steam, as it passes through the first coil, is heated and is distributed through the entire mass of oil as it escapes from the perforations in the second coil. The steam is regarded by Mr. Merrill as an important adjunct in this method of fractional distillation, as it acts mechanically by carrying forward the vapors into the condenser, and also prevents the overheating and "cracking" of either the oils or the vapors.

When the destructive distillation of petroleum commenced on a large scale, the slow distillation necessary to effect this decomposition led to an increase in the size of the stills until the enormous capacity of 2,000 barrels, or 80,000 gallons, was reached. These immense stills were built without covering, were freely exposed upon their sides and tops to the elements, and were heated by numerous fires, placed at equal distances from each other upon the circumference of the still, after the manner of the setting of the cheese-box still. These excessively large stills are not now being used. Refineries lately put in operation are equipped with stills holding about 1,200 barrels each.

Vacuum stills have been used to some extent, and have been employed especially in the United States by the Vacuum Oil Company, of Rochester, New York, in the preparation of the peculiar products of their manufacture. Of course the evaporation in these stills takes place rapidly and at the lowest temperature possible, insuring a fractional distillation, not a decomposition, of the oils.

CONDENSERS.—Large copper worms, similar to those used in distilleries, were at first used for petroleum stills. These were soon replaced by ordinary iron piping coiled in a cistern or tank of water, and still later very long, straight pipes were used with advantage in the use of water for cooling. Refineries lately built are provided with condensers of moderate length, 50 by 20 by 8 feet, in which there are numerous separate pipes, which receive the vapors at one end and discharge the condensed oil at the other. A condenser thus constructed may consist of forty separate 3-inch pipes, each 45 feet in length, giving an aggregate length of 1,800 feet, the oil and vapors, instead of all traversing the entire length of 1,800 feet, being divided into small portions, each of which is made to traverse the 45 feet, and is condensed. The ratio of exposed surface to cubical content is very much increased by this arrangement over a shorter pipe of larger diameter.

A very convenient arrangement for dividing distillates is shown in the section in Fig. 43. In this section *a* is the 2-inch pipe leading from the condenser, *b* is a pipe for uncondensed gases leading to the boiler furnace, *c* is the trap for holding back the gas, *d* is a wrought-iron box with a glass front *i i*, through which the flow of oil from the condenser can be observed. The glass front is on hinges, and can be opened for sampling the oils. From this box the oil passes into the pipes below, and is directed into one of the openings *g*, through which it enters the pipe *h h*, leading to the storage-tanks for distillate; *e e* are three-way cocks, and *f f* ordinary stop-cocks, by which the oil is directed to one of the six orifices *g*. By this arrangement, by simply opening or closing the cocks, the distillate can be directed to any one of six receptacles and be divided into as many different portions.

AGITATORS.—The agitators used at first were small tanks lined with lead, in which various mechanical contrivances were used to effect the thorough mixing of the oil with the chemicals. These lead-lined tanks were replaced by wrought-iron ones, and finally the method of agitating by mechanical means has been entirely superseded by agitation by means of injected air. The agitators in use in refineries lately constructed are high wrought-iron tanks of comparatively small diameter, holding several hundred barrels of oil, in which the most complete agitation is produced by a current of air injected by a blowing apparatus.

PUMPS.—The pumps used in refineries are many of them very powerful. Those used for pumping oil and water are of the Worthington or the Drake pattern, and consist of an engine and a pump combined. Some of these pumps are large enough to handle 2,500 barrels of crude oil an hour, but the majority are smaller. In addition, there are in use small blast-engines or air-pumps to force air into the agitators and into the acid-tanks. The latter are small lead-lined tanks, into which the acid is emptied from carboys or tank-cars. The acid is measured into the agitators by forcing it from the tank into the agitator under pressure of injected air.

PACKING.—Manufactured oils of all kinds are distributed to wholesale houses all over the country in tank-cars, but for the jobbing and retail trade they are packed in barrels and in tin cans. The barrels used at present hold from

a S. D. Hayes, Am. Chem., ii, 401; C. Cbl., 1871, 783; W. B., 1871.

48 to 50 gallons, and manufactured oils are estimated at 50 gallons to the barrel. The tin cans contain 5 gallons each, and are packed in wooden cases, each of which holds two cans. In the larger establishments the packages are filled by weight, as the bulk of the oil varies with the temperature and specific gravity of the oil, as may be seen at a glance at the table accompanying this report (see page 112). The filling of the 5-gallon cans is carried on at a square, revolving table. Ten cans are closely ranged along one side of this table and brought beneath ten funnels, which deliver oil to the cans until their weight stops off the oil by tipping a balance and closing a stop-cock. The ten cans are then swung out by giving the table a quarter revolution. While these cans were being filled another ten cans were placed upon the adjoining side of the table, and when the first were swung from under the funnels the second were brought into their places. While the second ten cans are being filled a third set are being placed upon a third side of the table, and a nozzle, with a cap that screws on and off, is placed in position for soldering over the orifice through which the first ten cans were filled. The table is again swung, the third set of cans are brought into position, and are then filled; the second set are supplied with nozzles, while the nozzles of the first set are soldered on and the fourth side is supplied with ten cans. Another swing of the table, and the fourth set are filled, the third supplied with nozzles, the second soldered, and the first removed, and a fifth set is put in their places. Several thousand cans can be filled in this manner at one of these tables in a single day.

SECTION 5.—DESCRIPTION OF AN ESTABLISHMENT IN WHICH THE PRODUCTS ARE GENERAL.

The plant consists of storage-tanks for crude material; stills, heated by fire, steam, and superheated steam; agitators; chilling-house for paraffine; boilers, engines, pumps; a laboratory; cooper and tin shop. The crude oil is delivered in pipes or tank-cars to the general storage-tanks and allowed to settle. From one to two per cent. of water separates. (a) About 300 barrels (12,000 to 13,000 gallons) of this oil are placed in a still and "live steam", *i. e.*, at 212° F., is admitted, and the distillation carried on until the distillate marks 60° B. With crude petroleum of 45° B. the amount of this distillate will be from 12 to 15 per cent., divided as follows:

A.

	Per cent.
1. "Crude gasoline", to 80°, about	½
2. "C" naphtha, 80° to 68°, about	10
3. "B" naphtha, 68° to 64°, about	2 to 2½
4. "A" naphtha, 64° to 60°, about	2 to 2½

1 is redistilled by dry heat, and yields from 90° to 83° gasoline, which is not treated; 83° to 80° is returned to crude gasoline.

2 is treated with 4 ounces of oil of vitriol to the gallon and washed with caustic soda, all cold, and then redistilled by steam from an alkali solution. Its average specific gravity is 70°, and it is known in the trade as benzine-naphtha.

3 and 4 are also treated with acid and caustic soda. The average specific gravity of 3 is 65° to 66°, and of 4 62°.

There remains in the still from 88 to 85 per cent. below 60°. This is transferred to cylindrical cast-iron stills with meniscus-shaped wrought-iron bottoms and distilled by direct heat, with 2 per cent. of soda solution of 14°. The distillate is thus divided:

B.

	Per cent.
1. Crude burning oil, from 58° to 40°, about	50
2. "B" oil, from 40° to 36°, about	20
3. From 36° downward, about	25
4. Cokings or residuum	3
5. Loss	2
	100

1 is treated with 4 ounces of oil of vitriol to the gallon and is agitated for half an hour. It is then drawn off from the tarry residue, and after being washed with water is again agitated for an hour with 2 per cent. of alkali solution, and is then drawn off and next day washed with a large amount of water, pumped into a fire-still upon a solution of soda equal to 4 per cent. of 14°, and distilled as long as the color is good, the amount usually being about 80 per cent. This distillate is the equivalent of "Downer's standard kerosene", and has a specific gravity of 45° and a fire-test of 125° F. The remaining 20 per cent. is run above 36° to crude burning oil (B 1), and below 36° to "finished machinery oil" C, to chill and press for paraffine.

2. "B" oil is distilled like 1 on soda lye. Of the distillate, above 36° goes to crude I; below 36° to the machinery oil C, to chill and press for paraffine.

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a As high as 13 per cent. of water has been obtained from residuum exported to England. It is not a legitimate mixture. C. N., xxx, 57.

3 goes to crude lubricating oil, and is treated with 4 ounces of acid to the gallon upon water at 212° F. for one hour, and is then distilled from a 2 per cent. solution of soda lye. Of this distillate above 40° goes to crude B 1, from 40° to 36° to B 2, from 36° downward, as long as the color is good, to machinery oil C, to chill and press for paraffine.

4 goes to coking-tanks.

C.—MACHINERY OIL, 36° AND DOWNWARD.

This oil is twice distilled and chilled in barrels packed in an ice-house for a week with ice and salt at 26° F. The crystalline *magma* is pressed in an hydraulic press and yields:

1. Crude scale paraffine (E).
2. Pressed lubricating oil of a specific gravity of 32°, which is partly sold as "spindle oil".
3. The portion not sold as spindle oil is placed in a still provided with coils for distilling with steam superheated within the oil itself. This still is heated with direct heat until the temperature has reached 250° or 300° F. Steam is then passed into a coil, which is immersed in the body of the oil, and is then allowed to escape into the oil through another coil, which is perforated, thus distributing the steam throughout the oil at the same temperature as the oil itself. Twenty to 30 per cent. of the lighter products, with all those having an offensive odor, ranging in specific gravity from 50° to 32°, are lifted from the still by the steam. Of this distillate, that between 50° and 40° goes to B 1, that between 40° and 32° to "crude mineral sperm" (D), and the oil left in the still is equivalent to "Merrill's deodorized neutral hydrocarbon oil", with a specific gravity of 29°. To remove fluorescence chromic acid is used instead of oil of vitriol.

D.—MINERAL SPERM ILLUMINATING OIL.

This is the trade-mark of a dense oil of 36° specific gravity, deprived of offensive odor, and adapted especially for light-house and locomotive lights. Any crude distillate from 40° to 32° is first treated with 4 ounces of oil of vitriol to the gallon, then washed with a solution of caustic soda, and distilled by direct heat over soda lye. It has a fire-test of 300° F. and but little odor, with a density of 40° to 34°, averaging 36°. Below 34° goes to machinery oil (C), to chill and press for paraffine.

E.—CRUDE-SCALE PARAFFINE.

The pressed scale equals three-quarters of a pound per gallon of the crude 32° machinery oil from the chilled mass described in C. To refine this the crude scale is melted in an open tank by live steam, blown in, with 1 per cent. of caustic soda lye, from which it is carefully drawn and then well mixed with 25 per cent. of "C" naphtha and put aside for three or four days in shallow metallic pans in a cold place. It is then again cut, bagged, and pressed.

No. 1 paraffine stock is remelted in "C" naphtha on alkaline lye, crystallized and pressed three successive times, and yields large crystals of paraffine, melting at 130° F.

No. 2 paraffine stock is treated in the same way, furnishing a product of less value in smaller crystals, melting at about 116° F., and is largely used by chewing-gum manufacturers. The oils expressed go to crude "C" naphtha

F.—COKINGS, SPECIFIC GRAVITY 28°.

These are redistilled over a 2 per cent. alkali solution, and furnish—

20 per cent. above 40° goes to B 1.

15 per cent. 40° to 36°, goes to B 2.

50 per cent. 36° and downward, as long as the color is good, goes to C.

10 per cent. cokings.

5 per cent. loss.

G.—SLUDGE (RESIDUES FROM WASHINGS).

The waste "acid sludge", 48° to 50°, is permitted to stand two days, and the oil rising upon it is drawn off ("sludge acid oil") and the acid disposed of. The sludge oil is then washed with the waste alkali and redistilled separately without fractions, yielding 80 per cent. of oil; coke and loss, 20 per cent. The coke is used as fuel, and the oil redistilled on alkali and fractioned as crude oil below 60°.

H.—AVERAGE PERCENTAGE OF COMMERCIAL PRODUCTS OBTAINED FROM CRUDE PETROLEUM OF 45° FROM NEW YORK, PENNSYLVANIA, OHIO, OR WEST VIRGINIA.

	Per cent.
Gasoline	1.0 to 1.5
"C" naphtha	10.0 to 10.0
"B" naphtha	2.5 to 2.5
"A" naphtha	2.0 to 2.5
	16.5
Illuminating oil	50.0 to 54.0
Lubricating oil	17.5
Paraffine wax = 4½ pounds per barrel	2.0
Loss	10.0
	100.0

The oils prepared by this process are all of the highest degree of excellence, and have commanded the confidence of consumers both in the United States and in all other civilized countries to a remarkable degree. There are two essential particulars in this process as a whole to which I desire to call attention. All destructive distillation is avoided so far as is possible, and great care is taken to render the different products pure as regards each other, and also as regards the effects of treatment. The products are essentially paraffine products, using that word in a generic sense to designate not only the paraffine wax, but the whole series of compounds to which it is related, from marsh-gas upward. The finishing of the burning oil by distillation over caustic soda is claimed, and I believe justly, to remove all of the substitution compounds of sulphuric acid that are only completely removed even by solution of caustic alkali when the oil is heated to a temperature above the boiling point of water. (*a*)

SECTION 6.—DESCRIPTION OF A MANUFACTORY WHERE NAPHTHAS, ILLUMINATING OILS, AND RESIDUUM ARE PRODUCED.

The following description is given after an inspection of one of the most complete establishments in the country, lately constructed and furnished throughout with an equipment of the most improved apparatus:

The oil is received in tank-cars, and an entire train is discharged at once into a 12-inch pipe, which runs the length of the siding between the rails and beneath the sleepers, connection being made with cocks underneath the car-tanks by union joints and hose. This 12-inch pipe discharges into a tank, from which the oil is pumped by a Drake steam-pump, handling 2,500 barrels an hour, which throws the oil either to the stills or to the storage-tanks, of which latter there are four, holding 35,000 barrels each. The capacity of this pump is not required for the storing of oil, but for the filling of the stills, of which there are nine, holding 1,200 barrels each. Three of these stills are cheese-box stills, and six are plain cylinder stills, 30 feet by 12 feet 6 inches, the former being set in one group, and the latter on a bench, side by side, like a bench of boilers. These stills are all covered with sheet-iron jackets, but are not otherwise protected or covered in any manner. The condensers are made in the manner described on page 163, with a large number of separate strands of pipe, which are immersed in a tank 50 by 20 by 8 feet. These strands enter a connecting pipe which emerges from the tank and enters a small building, where the discharge pipes from the nine stills are brought together side by side. Each discharge pipe terminates in a U-shaped gas-trap, and enters an iron box with a glass front, through which the flow of the oil from the pipe may be observed. The arrangement of the traps and the form of the boxes are shown in section in Fig. 43. The gas-pipes from the nine traps all connect with furnaces beneath the steam-boilers, where the gas, mixed with air, is burned after the manner of a Bunsen burner. The division of the distillates is effected by means of an arrangement of pipes and cocks shown in section in Fig. 43. Each of the nine boxes *d* (Fig. 43) discharge through this set of pipes, by which the distillate may be divided into six different qualities. These six different pipes connect under ground with the distillate tanks, which they enter at the bottom, and are sealed by the contents of the tanks. These nine sets of boxes and pipes are placed in a small building, lighted at night by an electric light, placed upon a pole at some distance off on the outside. The petroleum is put into the stills, and the crude naphtha is run off. Then that portion of the petroleum is run off which is necessary to prepare the distillate for "high-test" oils having a fire test of from 120° to 150°, as may be required, and these latter oils having been run off, the residue in the still is in a condition for "cracking". The fires are then slacked, and the distillation is run more slowly, a large amount of permanent gases being disengaged and burned under the boilers. Until the process of cracking is commenced the amount of gas disengaged is inconsiderable, so small in amount as to be scarcely worth the trouble of burning; but after cracking commences the gas generated is nearly sufficient to supply the fuel necessary for the boilers. The distillates are pumped into the agitating tank, which stands by itself, supported on a massive base of timber. It is about 40 feet in height and 12 feet in diameter. Twelve hundred barrels of distillate and 6,600 pounds of oil of vitriol are placed in this tank. The carboys of oil of vitriol are emptied into an air-tight, lead-lined tank, which is closed, and air is forced into it until a sufficient quantity of acid has been driven by the pressure into the agitator. The agitation is then carried on by forcing air into the agitator under a pressure of from 5 to 7 pounds. The acid being drawn off, the oil is thoroughly washed with water, then with a solution of caustic soda, and lastly with water containing caustic ammonia, the treatment with ammonia being supposed to complete the removal of the compounds of sulphuric acid. The oil is discharged from the agitator into settling and bleaching tanks, 40 by 5 feet, having a capacity of about 1,200 barrels each, through a perforated pipe standing perpendicularly in the center. By this process, which is called "spraying", the oils, particularly those that have been cracked, are brought up to "test" by the evaporation of the small percentage of very volatile oils that are combustible at a low temperature. These huge tanks are exposed beneath sky-lights, where the color of the oil is improved by the sunning, every particle of water or sediment settling at the bottom. From them the oil is pumped to storage-tanks in the barreling and canning house, where it is barreled in glued barrels or filled into 5-gallon cans, two of which are packed in a wooden case for shipment. From the packing-house the barrels and cases are put on board ships that lie at the adjoining

a I have drawn largely for this description upon Dr. J. Lawrence Smith in his report on petroleum to the Philadelphia Centennial Exhibition. Rep. Judges of Group III.

piers. This is the simplest process for manufacturing petroleum, consisting only of a single distillation; and the methods employed in the different manufactories throughout the country are either substantially that just described, or a combination with more or less of the processes described in the preceding section, or one or more of the special methods to be described in the section which follows.

SECTION 7.—MISCELLANEOUS PROCESSES.

REFINING CRUDE NAPHTHA.—There are several firms whose business consists mainly in refining crude naphtha, the larger portion of it being divided into gasoline and C, B, and A naphthas. In 1866 Dr. Henry J. Bigelow, of Boston, requested Mr. Joshua Merrill, of the Downer Kerosene Oil Company, to prepare the most volatile fluid possible to be obtained from petroleum. Mr. Merrill redistilled gasoline by steam heat, and condensed the portions that came over first with a mixture of ice and salt, obtaining 10 per cent. of the gasoline, equal to one-tenth of 1 per cent. of the original petroleum, in the lightest of all known fluids, having a specific gravity of 0.625 and a boiling point of 65° F. This fluid was named rhigolene by Dr. Bigelow. Its evaporation at ordinary temperatures is so rapid that a temperature of 19° F. below zero has been obtained by its use. Five or six hundred gallons have been prepared by the Downer company for use in surgical operations, but none was prepared by them during the census year.

A similar material, called cymogen, has been prepared in a similar manner by other manufacturers, and has been used as the volatile fluid in ice-machines.

The distillate separated as gasoline ranges in specific gravity from 90° to 80° B., and is used for the gas-machines that carburet air.

"C" naphtha includes the distillate between 80° and 68° B., and is used for varnishes, sponge lamps, paint, and naphtha street lamps. It is sold under the name of "benzine".

"B" naphtha includes the distillate between 68° and 64° B., and is also used for varnishes and paints.

"A" naphtha includes the distillate between 64° and 60°, and is used in the manufacture of floor-cloths and patent leather. Below 60° goes to illuminating oil.

Each of the different grades of naphtha is deprived wholly or in part of its disagreeable odor by being filtered through beds of gravel and wood or animal charcoal.

"MINERAL SPERM."—This is an illuminating oil prepared originally by Mr. Joshua Merrill, of the Downer Kerosene Oil Company, and now chiefly manufactured by that company, and is obtained by partially cracking paraffine oils and fractionating the lighter from the heavier products in Merrill's double-coil still or some similar contrivance. It has a fire test of 300° F. and upward, is an illuminating agent of great power, and is as safe from ordinary combustion as sperm oil. This oil is used in manufacturing establishments and on ocean steamers, and is a very suitable material with which to light steamers and cars designed for the conveyance of passengers. The amount produced during the census year was 16,544 barrels.

NEUTRAL LUBRICATING OILS.—These oils were also discovered by Mr. Merrill, as before described, and their superior quality soon led to their imitation and manufacture by other parties, although that gentleman protected his discoveries and invention by patent. Since the Downer company commenced the manufacture of these oils the general character of all of the mineral lubricating oils in the market has been greatly improved. The paraffine oils manufactured prior to this discovery were dark in color and rank in odor, but Mr. Merrill produced oils odorless and tasteless. Five per cent. of sperm oil mixed with 95 per cent. of Merrill's neutral oil could not be detected by either the odor or taste from pure sperm oil. An inspection of the tables representing the articles manufactured from petroleum during the census year will show that 79,465 barrels of paraffine oil are reported, all of which was greatly superior to the paraffine oil of 1865; of deodorized lubricating oils there were manufactured 70,415 barrels. These really superb oils are now being introduced into many manufactories by order of the insurance companies. The value of having a deodorized lubricating oil can be fully realized when it is stated that experiments have shown that when a heavy hydrocarbon containing so little as 1 or 2 per cent. of light offensive oil is employed in a warm apartment as a lubricator of machinery the entire atmosphere of the apartment will be impregnated by the pungent and disagreeable odors of these volatile products. Before the employment of these odorless oils this was a great inconvenience in factories. (a)

Mr. Merrill prepares lubricating oils by subjecting an ordinary paraffine distillate, from which the paraffine has been removed by chilling and pressing, to fractional distillation in his double-coiled still, but oils may be prepared that are similar, though not fully equal, to his in an ordinary still, provided care is taken not to crack them.

FILTERED OILS.—A very superior quality of lubricating oil is prepared by reducing petroleum and filtering the reduced residue through beds of animal charcoal. The oil is reduced to the proper degree of volatility and specific gravity and then filtered. These oils sustain a very high reputation, but precisely what relation they bear in quality to the neutral oils obtained by distillation and treatment I cannot state.

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a *Loc. cit.* Rep. of Judges of Group III, p. 153.

VACUUM OILS AND RESIDUES.—Vacuum oils are also prepared in stills for a great variety of purposes. Those most dense and with highest boiling points are prepared for oiling the interior of steam cylinders; those less dense for journals; and a less dense oil is used extensively for oiling harness and harness leather. Very dense residues prepared in vacuum stills are filtered while hot and very fluid through beds of animal charcoal, the resulting product being an amber-colored material of the consistence of butter and nearly destitute of odor. These residues are largely used as unguents under the name of cosmoline, vaseline, petrolina, etc. The details of their manufacture are difficult to obtain, for the reason that the manufacturers are engaged in suits involving patent rights to peculiar processes of manufacture and peculiar apparatus for effecting the filtration, which necessarily must be carried on at a sufficiently high temperature to insure complete fluidity of the material. These preparations will be further noticed under the chapter devoted to petroleum in medicine.

It is believed that but few, if any, general methods of any importance pursued in the manufacture of petroleum have been omitted in this chapter. It is a subject, however, embracing multitudinous details and carried on under conditions of great diversity, incident to the location of the business and the peculiar character of the crude oil used or the products which the manufacturer wishes to prepare.

CHAPTER IV.—PARAFFINE.

SECTION 1.—HISTORY.

Wagner's *Berichte* for 1869, in an historical notice upon paraffine, says:

The *Aerztliche Intelligenzblatt*, of Munich, contains the following notice: "The opinion universally held that the chemist Karl Freiherr von Reichenbach, who died in his eighty-first year, of old age, at Leipzig, January 19, 1869, was the first to investigate the paraffines, deserves the following corrections or amendments. In 1809 these bodies were observed by John Nep. Fuchs in Landshut in the petroleum of Tegernsee, and in 1819 Andrew Buchner, sr., produced them in a pure state from the oils. Buchner describes their peculiarities under the name of 'mountain' fats, whose identity with paraffine was established later (1835) by v. Kobell beyond doubt. Unqualified merit, however, belongs to Reichenbach as having first discovered paraffine in the products of the dry distillation of wood and other organic bodies." Reichenbach remains the discoverer of paraffine notwithstanding the fact that, beside Fuchs and Buchner, Saussure and Mitscherlich investigated a fatty body found in certain petroleums and tars which after the discovery of paraffine proved to be identical with this body. In all of these conditions the discourse was upon paraffine as an *educt*, and not as a *product*. Technology distinguishes the former from the latter through the name of *Belmontin*. He who first considered fossil paraffine can upon no condition lay claim to the honor of the discovery. In Moldau and in Galicia fossil paraffine has been used for centuries in making candles, as also on the Caspian sea and in the Caucasus. (*a*)

It appears from this statement, which is in accord with numerous authorities, that fossil paraffine has been known in Europe from time immemorial, and also that paraffine, as a recognized constituent of certain bodies of organic origin, was discovered by Reichenbach in 1830, (*b*) and named by him from *parum* and *affinitas*, indicating that paraffine is destitute of chemical affinity; in other words, that it is neutral, having neither acid nor alkaline properties. In the following year Christison, of Edinburgh, made known his discovery of paraffine in the petroleum of Rangoon. (*c*) He at first called it *petroline*, but after learning of Reichenbach's discovery he admitted its identity with paraffine. In 1834, Gregory published an article on paraffine and eupion and their occurrence in petroleum, in which he says:

It follows that there are some kinds of naphtha (petroleum) which contain paraffine and eupion, and are consequently the results of destructive distillation. (*d*)

In 1835, Kobell independently mentions paraffine as a constituent of petroleum. (*e*) In 1833, Laurent showed that oil distilled from shale in the environs of Autun contained paraffine. (*f*)

Although Reichenbach distilled coal in considerable quantities, and had at his disposal the resources of the immense establishment of "mines, iron furnaces, machine-shops and chemical works, etc.," on the estate of Count Salm at Blansko, Moravia, of which he was superintendent, he cannot be said to have produced paraffine on a commercially successful basis. This work was performed by Selligue, whose inventions formed the foundation upon which the technology of coal-oil and petroleum has been built. The following digest of the labors of Selligue is taken from the review of Dr. Antisell's work on photogenic or hydrocarbon oils by Professor F. H. Storer: (*g*)

In 1834 we find for the first time an article describing the process of Selligue, (*h*) although it would appear from the statements of this chemist and of others that his attention had been directed to the subject of distilling bituminous shales several years earlier.

a W. B., xv, 709, 1869.
b *Jour. für Chem. u. Phys.* von Schweigger-Seidel, 1830, lix, 436.
c Trans. Roy. Soc. of Edinburgh, xiii, 118; *Repertory of Patent Inventions*, 1835 (N. S.), iii, 390.
d *Ibid.*, xiii, 124; *Ibid.* (N. S.), iv, 109.
e *Jour. f. Prak. Chem.*, v, 213.
f *Ann. de Chim. et de Phys.*, liv, 392.
g Am. J. S., xxx, 1860.
h *Journal des Connaissances Usuelles*, Dec., 1834, p. 285; Dingler, lvi, 40.

* * * In 1834, '35, and '36 Selligue was principally occupied with his process for making water-gas. (a) * * * In the following year we again find Selligue before the academy, requesting that body to appoint a committee to examine the merits of his new system of gas-lighting; his process of distilling bituminous shales on the great scale by means of apparatus, each one of which furnishes from 1,000 to 1,400 pounds of crude oil per day—this being about 10 per cent. of the weight of the shale employed, and being almost all that exists in the raw material; also of his process of separating various products from the crude oil, some of which are applicable to the production of gas, others to ordinary purposes of illumination, and others to different uses in the arts. (b) This petition was referred to a committee of three, Thénard, D'Arcet, and Dumas, who reported in 1840. (c) * * * In 1838 Selligue obtained a new patent "for the employment of mineral oils for lighting", (d) which, it should be observed, claims only to be an improvement upon that of Blum and Moneuse. * * *

On the 27th of March, 1839, Selligue specifies certain additions and improvements to the preceding patent. In alluding to the use of his oils in the treatment of cutaneous diseases he speaks of the three large establishments for the distillation of bituminous shale which he has erected in the department of Saône et Loire, and mentions the fact that the oil (crude) is furnished at the rate of about 2 cents (10 centimes) per pound. (e) * * * The clearest of all Selligue's specifications, however, is that of the patent granted him March 19, 1845, for the distillation of bituminous shales and sandstones. (f) After describing the various forms of apparatus used in distilling, into one of which superheated steam was introduced, he enumerates the products of distillation as follows: I. A white, almost odorless, very limpid mineral oil, somewhat soluble in alcohol, which may be used as a solvent, or for purposes of illumination in suitable lamps. II. A sparingly volatile mineral oil of specific gravity 0.84 to 0.87, of a light lemon color, perfectly limpid, almost odorless, never becoming rancid, and susceptible of being burned in ordinary lamps, of constant level (à réservoir supérieur), with double current of air, a slight modification of the form of the chimney and burner being alone necessary. This oil can also be mixed with the animal or vegetable oils. Oils thus prepared do not readily become rancid, nor do they congeal easily when subjected to cold. III. A fat mineral oil, liquid at the same temperature as olive oil. This oil contains a little paraffine; it is peculiarly adapted for lubricating machinery, and has an advantage over olive and other vegetable oils, or neat's-foot oil, in that it preserves its unctuosity when in contact with metals and does not dry up. It saponifies easily, and forms several compounds with ammonia. IV. From the oils I, II, and III I extract a red coloring matter which can be used in various arts. V. White crystalline paraffine, which needs but little treatment in order to be fit for making candles. This substance does not occur in very large proportion in the crude oil, and the proportion varies according to the different mineral substances upon which I operate. There is but little of it in petroleum and in the oil obtained from bituminous limestone. I often leave a great part of the paraffine in the fat oil and in the grease, in order that these may be of superior quality. VI. Grease. This grease is superior to that of animals for lubricating machinery and for many other purposes, since it does not become rancid, and remains unctuous when in contact with metals. VII. Perfectly black pitch—very "drying"—suitable for preserving wood, metals, etc. VIII. An alkaline soap obtained by treating the oils with alkalies. IX. Sulphate of ammonia. X. Manure prepared by mixing the ammoniacal liquor or the blood of animals with the crushed fixed residue (coke) of the shale. XI. Sulphate of alumina from the residue of the shale. In describing the methods of purification proposed by Selligue we shall make no attempt to follow their various details, our limited space compelling us to content ourselves with only the broadest generalities. Selligue sets forth at length two methods:

1st. A cold treatment, which consists in agitating the oils with sulphuric, muriatic, or nitric acid. This agitation should be thorough, he says, and should be continued for a longer or shorter time, according to the nature and quantity of the matter treated. Here follows a description of his agitators. After several hours repose the oil may be decanted, except from muriatic acid, in which case more time and a larger amount of acid is required. After the oil has been thus separated from the deposit of tar, the acid remaining in it must be neutralized by means of an alkali. "I prefer," says Selligue, "to employ the lye of soap-boilers marking 36° to 38°, since it is easy of application and produces a sure effect. I thus precipitate together the coloring matter and the tar, which would otherwise have remained in the oil. The oil is then decanted; if it is the first distillation of the crude oil, I do not allow the mixture to subside entirely, preferring to leave a portion of the alkali mixed with the oil and to distill off only three-fourths of the latter. * * * When the soda lye—in quantity slightly greater than is necessary to neutralize the acid—is added, the liquid must be agitated violently, in order that each particle of the oil may be brought in contact with the alkali; and this agitation must be continued until the color of the oil undergoes change. The oil becomes less odorous and less highly colored after each such 'cold treatment'. After having been allowed to separate from the lye, the oil is decanted off; if it has not lost much of its color the process has been badly conducted. It must be stated that the oil must not be agitated several times with the alkali, for by so doing the dark color of the oil would be restored. * * * As for the residues of the soda treatment", continues Selligue, "they should be allowed to stand at rest during some days beneath a portion of oil, which will protect them from contact with the air. The clear lye at the bottom being then drawn off may be used for other operations, while the remainder is a soap containing excess of alkali. By adding to it a little grease a soap can be made, or by adding water grease may be separated. This grease is similar to that used for wagons."

2d. A warm treatment that follows the cold, and consists of a series of fractional distillations—special operations for the purification of the "light stuffs" being resorted to. For the details of these we must refer to the original specification of Selligue—a truly classical document—which should be read by every one interested in the manufacture of coal-oils (or petroleum). (g) * * * As for paraffine, Selligue obtained it by subjecting the oil to a low temperature, in order that this substance might crystallize. The mixed oil and paraffine was then thrown on fine metallic filters, through which the oil flowed while the paraffine was separated. Or one may separate the oil, he says, by imbibition, but this occasions a great loss of oil, and also requires more labor.

These successive patents, extending over a period of about fifteen years, show not only that Selligue was a complete master of this department of technology, on the general principles of which but little improvement has since been made, but also that, prior to 1845, this industry had become important and extensive in France.

In England no commercial importance appears to have attached to the paraffine-oil industry until 1850, when James Young and his associates, Messrs. Binney and Meldrum, established the extensive works at Bathgate, from

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a See 7 patents in *Brevets d'Invention*, lxx, 169. Of these patents two are dated 1834, two 1835, and three 1836. For a description of his process of gas-making, see also *Bul. Soc. d'Encouragement*, Oct., 1838, p. 396, or Dingler, lxxi, 29.

b *Comptes-Rendus*, 1838, vii, 897.

c *Ibid.*, x, 861, Dingler, lxxvii, 137.

d *Brevets d'Invention*, lxviii, 395.

e *Comptes-Rendus*, ix, 140; *Ann. der Pharmacie*, v. Wöhler u. Liebig, xxxii, 123.

f *Brevets d'Invention* (N. S.), loi du 5 *Juillet*, 1844, iv, 30.

g A tolerably accurate English translation of this important patent may be found in the specification of A. M. B. B. Du Buisson, 1845, specification No. 10,726 of the English patent office.

the success of which has followed the Scotch paraffine and mineral-oil industry, which, in 1878, produced from 800,000 tons of 2,000 pounds each of shale 30,000,000 gallons of crude oil. From 8,040,000 gallons of this oil was made: (*a*)

	Value.
500,000 gallons naphtha	$40,000
4,000,000 gallons burning oil	320,000
1,035,000 gallons heavy oil	82,000
200,000 gallons medium oil	16,000
Paraffine	62,000
Sulphate of ammonia, 82 per cent. products	23,000
	543,000

Specific gravity of the naphtha	0.725
Specific gravity of the lamp-oil	0.805
Specific gravity of the medium	0.840

SECTION 2.—SOURCES OF CRUDE PARAFFINE.

Crude paraffine is found fossil in Galicia, Roumania, the Caucasus, the neighborhood of the Caspian sea, and in the Sanpete valley in Utah. In all of these localities, except the last, it is found in a formation that yields petroleum and also contains paraffine. Paraffine is also a constituent of a large majority of the different varieties of petroleum found upon the earth's surface, and also of the asphaltums that occur in injected veins, such as albertite, grahamite, and the asphaltum of Cuba. As a product of destructive distillation paraffine is obtained from all kinds of bituminous coal, shales, lignite, peat, wood, and animal remains, provided the distillation is conducted at a sufficiently low temperature.

The fossil paraffine or ozokerite of Galicia is principally obtained in Boryslaw and Stanislow in the Miocene of the foot-hills of the northern slope of the Carpathians; also at Slanik, in Moldavia, near mines of rock-salt and coal. In 1875 the amount produced in these two localities was about 44,000,000 pounds. The "earth-wax" occurs partly in regular beds and partly in pockets, from which it is obtained in small pieces or masses of several hundred pounds weight. The beds containing the mineral are reached by shafts from 130 to 260 feet in depth, from which the exploitation is carried on by tunnels, as in ordinary mining. These shafts generally pass through gravel and bowlders from 25 to 30 feet, and then through blue loam and plastic clay. In this clay, at a usual depth of from 140 to 150 feet, the "earth-wax" is found in layers of from 1 foot to 3 feet thick, the purest being of a honey-yellow color, and of the hardness of common beeswax. Much of it, however, is in small pieces, which must be separated from the gangue, the smallest pieces being obtained by washing. The purer qualities, on being melted, yield a prime "earth-wax", which is manufactured into "ceresine." The poorer varieties are dark-colored, some of it being soft, containing petroleum, and some of it being hard like asphaltum. These poorer qualities are used for the manufacture of paraffine. Rarely pieces are found which are very compact and as hard as gypsum, fusing above 100° C., and, like many specimens of petroleum, are dichroic—dark-green in reflected light and pure yellow in transmitted light.

As stated above, the crude ozokerite is separated from the gangue by melting and worked into paraffine or ceresine. The "trying" is effected either by direct fire or by steam. In the former case, the ozokerite is placed in iron kettles about one and one-half meter in diameter by one meter in height, melted, drawn off, and the residue boiled with water, when all the ozokerite will rise to the surface of the water. In the latter case the melting is done by steam in the same manner as with paraffine or stearine, and needs no further description. The "tried" ozokerite is clarified by allowing it to settle for several hours and then poured into iron molds. It is shipped in this form, without any further packing, in pieces weighing from 50 to 60 kilograms (110 to 130 pounds). There are principally two kinds of commercial ozokerite, prime and second. Prime "wax" ought to be as free as possible from earthy impurities, and in small, transparent, greenish-brown to yellow pieces; the lighter in color and the more transparent the better it is. "Second wax" is dark brown, almost opaque, occasionally containing a great deal of earthy impurities, and is generally much softer than the prime. Both are used in the manufacture of either paraffine and illuminating oils or ceresine. The manufacture of paraffine from ozokerite is effected by distillation over direct fire from iron retorts with flat bottoms containing from 1,500 to 2,000 pounds. The product of the distillation are: (*b*)

	Per cent.
Benzine	2 to 8
Naphtha	15 to 20
Paraffine	36 to 50
Heavy (lubricating) oils	15 to 20
Coke	10 to 20

The paraffine is pressed, treated with sulphuric acid and caustic soda, filtered through paper and fine animal charcoal, and made into candles. The naphtha is purified in the usual way, and the heavy oils are sometimes subjected to fractional distillation, but mostly shipped as such to Vienna. The manufacture of "ceresine" consists of the removal of the impurities from the "earth-wax" by the aid of sulphuric acid and animal charcoal; but only the best kinds of ozokerite are used. The different processes are kept secret, and are also protected by patents. In general the ozokerite is melted with concentrated sulphuric acid, and the residue from the manufacture of yellow prussiate pressed, treated again with prussiate residue and filtered. One hundred parts good prime "earth-wax" yield sixty to seventy parts white wax, which in its properties very closely resembles white beeswax, and is called "ceresine". It is either further purified by repeated treatment with acid and prussiate residue, or colored with gamboge or alkanet, and thereby made to resemble common beeswax.

a Hübner's Zeitschrift, 1879, 12; W. B., 1879, 1170.

b This is manifestly a cracking process, and it is evidently a somewhat rude method of treating such a valuable substance. Distillation by steam would be much better.

In the manufacture of ceresine only sulphurous acid and press residues are obtained, the former of which escapes into the air, but might be utilized, thus reducing the cost considerably. The consumption of sulphuric acid in Boryslaw alone is said to amount to 2,200,000 pounds a year. The prussiate residues are obtained from the lixiviation of the crude prussiate in Moravia. Comparatively only a small quantity of earth-wax is worked in Galicia, and is shipped principally to England, Moravia, and Vienna. The ceresine is exported in large quantities to Russia, where it is sold as beeswax, a little of which is melted with it in order to impart to it the characteristic odor. Good ceresine is hardly to be distinguished from beeswax. The best method is the following: 1. Ceresine is not as easily kneaded between the fingers and becomes brittle more readily than beeswax. This test is, however, doubtful if the sample is a mixture of the two. 2. Ceresine is scarcely attacked by warm concentrated sulphuric acid, whereas beeswax is completely destroyed by it. By this test the quantities of beeswax and ceresine can be determined in a mixture of both. In many cases ceresine can be employed in place of beeswax. It is sold at $32 to $40 per 100 kilogrammes (16⅔ cents per pound) in Vienna, whereas the price of the commercial earth-wax varies from $10 to $12 per 100 kilogrammes (5 cents per pound). The whole exploitation of the ozokerite is in the hands of the Jewish population. (*a*)

The ozokerite deposits of Utah have not yet been worked sufficiently to demonstrate their importance. The crude material is of about the consistence of paraffine, and is of a jet black color, and furnishes, when purified, a pure white paraffine.

The question whether paraffine is or is not a constituent of petroleum has been widely discussed. I am not prepared to assert that crystallizable paraffine is a constituent. I have seen crystals of paraffine in petroleum that came from the wells of the Economites opposite Tidioute that I had no reason to suppose had ever been heated, or, in fact, manipulated in any manner, except to be put into barrels; yet I cannot positively assert that such was the case. Amorphous paraffine is certainly a constituent of many petroleums, and is readily obtained where petroleum is carefully distilled until the residue has the consistence of paste when cold. The amount of reduction necessary varies with the source of the petroleum used. A sample from the southeastern border of the Pennsylvania petroleum field was of an amber color, and of nearly the consistence of honey from suspended paraffine. The oil of the Bradford field is remarkable for the amount of paraffine it contains as compared with other oils of the Pennsylvania region. This peculiarity occasions a great deal of trouble with flowing wells, as the pipes become clogged with paraffine so completely as to stop the flow of oil. This is no doubt in part occasioned by the fractional condensation of the paraffine in consequence of the extremely low temperature produced by the rapid evaporation of the more volatile portion of the petroleum when it is relieved from the enormous pressure to which it is subjected in the rock. This extremely low temperature, which has been known to plug a well with ice and to produce ice under the sun of a hot summer's day, evidently condenses the paraffines having the highest melting point, and allows those more fusible to remain dissolved in the oil. (*b*) As regards the practical working of petroleum, it is of little importance whether the paraffine is an educt or a product, for if the paraffine is not already a constituent of crude petroleum, the heat required for distillation develops it. The amount of paraffine, however, that any given sample of petroleum contains or will yield is a matter of the greatest importance if the crude oil is to be made into illuminating oils. The crude oils of Butler and Armstrong counties are much more valuable for that purpose than those of McKean county, because they contain more of the members of the paraffine series of the proper specific gravity for illuminating oils and less of the dense, heavy oils and solid paraffine that have to be cracked before they can be used for illumination.

In 1849 a Mr. Reece obtained a patent for distilling paraffine from Irish peat, and works for its production were established near Ashby. While the method of treating the peat was entirely successful, the enterprise, on account of the small amount of material it was capable of yielding, was a commercial failure. It is proper to state here, however, that acetic acid and ammonia, as well as paraffine, were expected to be obtained in commercially valuable quantities. The following statement will give an idea of the proportion of these articles yielded by the peat. On the first distillation the peat yielded:

	Per cent.
Watery matters	30.614
Tar	2.392
Gases	62.392
Ashes	4.197
	99.595

The watery matters and tar yielded:

	Per cent.
Ammonia	0.287
Acetic acid	0.207
Naphtha	0.140
Volatile products	1.059
Paraffine	0.125

a J. Grabowsky, *Am. Chem.*, vii, 123. Hübner's Z., 1877, 83.

b Various methods have been suggested for removing this paraffine from the pipes. It is only slightly soluble in benzine, and neither acids nor alkalies attack it, and other solvents are equally ineffectual. Metallic mercury has been used, which must act mechanically by its weight. A plan to burn it out of the pipes by supplying a stream of oxygen has been recommended, but what degree of success, if any, attended its use I have not learned. The most common method pursued in the oil region is to pull up the pipes and blow out the plug of paraffine with steam. The pipes are often found plugged solid for hundreds of feet.

Fifty tons of peat yielded 125 pounds of paraffine, an amount too small to admit of a profitable enterprise. (*a*) The peat of Hanover yields more than 300 pounds of paraffine to 50 tons.

J. J. Beitenlohner gives the following results of the manufacture of paraffine from peat-tar. The locality of the peat is not given, nor is the amount of tar yielded:

By fractional distillation:	Per cent.
Crude and chemically combined oil	35.3
Crude paraffine in mass	48.2
Coke	10.4
Gas	6.1
	100.0

The results of the purification of the paraffine with sulphuric acid and lye are:

	Per cent.
Paraffine	76.3
Loss by sulphuric acid	12.2
Loss by lye	9.4
Loss by washing	2.1
	100.0

The paraffine thus obtained is subjected to distillation, the result being:

	Per cent.
Oils	25.5
Paraffine	66.5
Coke	2.6
Gas	5.4
	100.0

The paraffine is then refrigerated and pressed, and from it are obtained:

	Per cent. in winter.	Per cent. in summer.
Coke	21.6	18.2
Oils	75.3	78.3
Loss	3.1	3.5
	100.0	100.0

This paraffine is then digested in fuming sulphuric acid, but remains soft and unctuous. (*b*) The distillation evidently cracks it.

In an elaborate research upon the products of the dry distillation of Rhenish shale and Saxony and Thuringian brown coal, H. Vohl gives the following table, showing the comparative value of shales, brown coal (lignite), and peat as sources of paraffine: (*c*)

Raw material.	Light oil or photogen: sp. gr. 0.820.	Heavy gas or lubricating oil: sp. gr. 0.860.	Paraffine.	Asphalt.	Creosote and loss by refining.
Shale:	*P. cent.*	*P. cent.*	*P. cent.*	*P. cent.*	*P. cent.*
English	24.285	40.000	0.120	10.000	25.595
From the Romerickeberg mine	25.688	43.000	0.110	12.030	19.166
From Westphalia	27.500	13.670	1.113	12.500	45.300
From Oedingen on the Rhine	18.333	38.333	5.000	13.333	25.001
Brown coal from—*					
Aschersleben, No. I	33.500	40.000	3.330	18.100	5.070
Aschersleben, No. II	20.500	43.600	6.510	19.567	9.823
Frankenhausen	33.410	40.063	6.730	17.321	2.476
Münden	17.500	26.213	5.063	18.079	32.545
Oldisleben	17.721	26.600	4.430	17.526	33.722
Cassel, No. I	16.428	27.142	4.286	14.290	37.853
Cassel, No. II	16.666	21.052	5.263	13.163	43.855
Bavaria (von der Rhon)	10.625	19.375	1.250	16.000	51.850
Tilleda	16.666	18.055	4.444	11.111	49.722
Brown coal from—Continued.	*P. cent.*	*P. cent.*	*P. cent.*	*P. cent.*	*P. cent.*
Harbke, No. I	15.555	11.111	3.555	22.222	47.555
Harbke, No. II	16.666	11.765	2.941	20.000	48.627
Stockheim, near Düren	17.500	26.630	3.260	16.000	36.710
Bensberg, near Cologne	16.360	19.535	3.463	13.173	47.461
Peat from—					
Celle	34.600	36.000	8.010	11.540	9.850
Coburg	20.625	26.578	3.125	17.190	32.482
Damme	19.457	19.547	3.316	17.194	40.486
Neuenhaus, heavy	17.983	19.640	5.360	16.071	40.945
Neuenhaus, light	14.063	18.230	5.209	18.750	43.748
Zurich	14.400	8.666	0.424	42.424	35.080
Russia (Rostokina, near Pasjkina)	20.390	20.390	3.367	25.658	30.105
Bottross, in Westphalia	11.000	19.489	2.256	26.000	41.255
Neuwedel, Prussia	14.180	18.266	3.102	28.260	30.241

* These "brown coals" are lignites, nearer peat than coal.

a Frederick Field, J. S. A., xxii, 349, 411; *Am. C.*, v, 169. *b* *Jour. de l'Éclairage au Gas*, 1872, No. 5, Am. C., ii, 315. *c* W. B., iii, 459.

The paraffine oil industry of Scotland has already been noticed. Its present success, notwithstanding the low price of petroleum products, is mainly due to the heavy oils and paraffine produced. While I cannot indorse all the claims that are made for Mr. Young as the first inventor, as the process which he patented corresponded to that used by Selligue many years before, there is no question that he deserves the credit of having placed the paraffine industry on a solid commercial basis in Great Britain at a time when the discovery of petroleum in such vast quantities in Canada and the United States would seem to have rendered such an undertaking impossible.

At the date (1860) at which petroleum was first an article of commercial importance, paraffine and paraffine oils were being produced in the United States and Great Britain from the so-called Boghead coal, albertite, and grahamite, together with several rich cannel coals. The deposits of the three minerals above mentioned have been worked out. The last establishment in the United States using anything but petroleum was the Union Coal and Oil Company, of Maysville, Kentucky, which was operated upon the rich cannel coal of Cannelton, West Virginia, on the Great Kanawha river. It ceased operations in 1867. The deposit of Boghead mineral was worked out in 1872, since which time the extensive paraffine oil works of Scotland have been run on shale. On the continent of Europe, in Saxony, Thuringia, and Austria, an extensive and very valuable industry is conducted with shale and brown coal as the raw material. In the United States, beside our deposits of cannel and bituminous coals of enormous extent, we have thousands of square miles of shales that will furnish millions of barrels of distillate for use after our 200,000 square miles of petroleum fields shall have been exhausted.

Section 3.—PREPARATION OF PARAFFINE.

The preparation of paraffine from petroleum has already been described on page 165, and the treatment of the crude oils distilled from shale or coal is substantially the same, with the exception that more sulphuric acid and more numerous distillations are employed. While crude shale oils and petroleum are very similar fluids, the shale oil is much more impure and more expensive to refine. Distillation and treatment with sulphuric acid and soda lye are, with some variation in the details, the methods upon which the technologist in paraffine must rely. The subsequent treatment of the crude paraffine scales is subject to considerable variation, and an article quite variable in its properties is the result. The ordinary method of purification consists in dissolving about 2,000 pounds of crude paraffine in 80 gallons of "C" naphtha by heat, refrigerating in shallow metal pans and pressing; but this method is attended with considerable loss of naphtha, and some danger from accidental ignition. To obviate this a process was invented for treating the paraffine cold, by which it was either pulverized and then dissolved in naphtha, or the cake and naphtha were ground together into a paste and then pressed. After this grinding and pressing has been repeated a sufficient number of times, the solid wax is melted in a still with steam blown in until no naphtha comes over with the condensed water. From 3 to 5 per cent. of animal charcoal is then added, and while the mass is kept melted the charcoal is allowed to settle. As the finest particles of charcoal remain diffused through the wax, the whole is filtered hot through a wire-gauge filter, which is lined with flannel and filter paper, the filtrate passing as colorless as distilled water. (a)

The use of these successive solutions in naphtha is to remove the fluid oils from which the paraffine first crystallizes, which are more readily soluble in the naphtha than the paraffine itself. Mr. John Fordred in 1871 sought to accomplish the removal of these oils by kneading the paraffine with or in a slightly alkaline solution. After melting and clarifying a ton of paraffine and casting it into thin cakes of about ten pounds each, these cakes are placed in a bag, end to end, and warmed until they become plastic. The bag is then placed in a kneading machine, which is supplied with a solution of equal parts of soft soap and water at a temperature of about 100° F. On setting the machine in motion the oil and coloring matter are dissolved in the soap solution. Solutions of carbonated and caustic alkalies, both alone and mixed with soap, rosin soap, and even warm water itself, are found to answer the purpose. (b) Another patent claims economy in operation and safety in the use of material. A tank 12 by 6 by 2½ feet is provided with partitions, which separate it into V-shaped cells, 2½ inches wide at the top and 2 inches wide at the bottom. These cells are 1 inch apart, and start 9 inches from the top of the tank and stop 2 inches from the bottom. A grating is provided, that rests upon the top of the cells, the bars of which are 1½ inches apart. Free or closed steam-pipes are placed in the bottom of the tank, and water is filled in to a depth of 6 inches. Crude paraffine is filled into the cells and the grating secured to prevent its floating. Water is then run in until it rises to within two inches of the top of the tank, and steam is turned on until the temperature reaches within 10° of the melting point of the paraffine being treated, when it is turned off and the entire mass is allowed to become of a uniform temperature. Steam is then again turned on and the temperature very slowly (through at least 4 hours) brought to within 2° of the melting point of the paraffine, when the soft portions that have risen are skimmed off. The water is then drawn off to the top of the cells and the paraffine is melted and allowed to cool slowly through the night, when the operation is repeated. This is continued until paraffine is obtained of the required hardness, while the soft portions are returned to the crude paraffine. The hard paraffine is then melted with 7 per cent. of powdered commercial ivory-black in a steam-jacketed pan for four or five hours, until the

a Patent of Ed. Meldrum, No. 1646, 1867.

b Patent No. 1858, 1871.

whole of the ivory-black is precipitated, when it is drawn off and cast into cakes. (*a*) Another process requires the paraffine to be clarified by settling and being cast into cakes, which are allowed to cool very slowly, in order that the crystals may form of large size. The cakes are then placed on tiles or other absorbent material and heated nearly to their melting point. The fluid and easily fusible portions are melted and flow from the crystals and are absorbed by the tile. This process may be repeated as many times as may be desired, and the paraffine may then be bleached with bone charcoal or by any other means. (*b*)

By whatever method the paraffine may be freed from the fluid and the fusible impurities, it is not white, and is afterward subjected to a bleaching process. One method has already been described; another requires that the melted paraffine be agitated in a tank by a current of air with from 5 to 10 per cent. of strong sulphuric acid, care being taken to remove the sulphurous acid evolved by a suitable ventilating apparatus. This agitation is carried on for several hours, until the experience of the operator shows the treatment to be sufficient, when the tarry mass is allowed to subside through several hours. The still slightly-colored paraffine is then digested with animal charcoal, the last traces of which are removed by filtering through a steam-jacketed filter. The apparatus by which this filtration is performed is thus described by L. Ramdohr in Dingler's *Polytechnic Journal*, 1875:

After paraffine has passed through all other stages of the purifying process, it must finally be decolorized by means of charcoal. The use of a permanent filter (eines stehenden) filled with granulated charcoal is not to be recommended for many reasons.

The filtering process must take place at a temperature of not less than from 70° to 80°; the filter also must be heated with steam, which, on account of the large dimensions, would require incommodious and expensive apparatus. But particularly against the use of granulated charcoal stands the fact that a greater part of the paraffine is retained by the charcoal, which can only be partly collected again through burning of the coal, which always is united with a considerable amount of decomposition (products) of the paraffine. But paraffine is so valuable that its manufacture cannot suffer such a great loss in material. Consequently the decolorization of paraffine takes place in a much simpler way with a fine, pulverized, and, where it is possible, freshly-heated charcoal, which usually becomes mixed with the paraffine by agitation with a wooden mixer, and the greater part of it thereupon very quickly settles to the bottom.

The fine particles of coal, notwithstanding, remain suspended a long time in the fluid paraffine, and are even not entirely removed after a day's rest, so that the paraffine must be completely cleared by filtration through paper. Paraffine that is not filtered is of a smutty gray color. In most of the paraffine manufactories I have found the arrangement of filter paper to be very primitive, and the mixing apparatus separated or divided by the filtering apparatus, so that a continuous scooping over of the paraffine to be filtered upon the filter and a continuous addition of the latter was necessary. Consequently, I give the following description of a mixing and filtering apparatus constructed by me, which I have used in two instances many years with the best results.

This has the following peculiarities in its arrangement: 1. The mixing of the paraffine with bone-black does not take place by the hand or through a mechanical stirring contrivance, but through a warm current of air previously blown into the apparatus. 2. The paraffine treated with bone-black flows of itself into the filter paper placed in a glass funnel, and after the influx has once been regulated the control of the entire apparatus by the workman is scarcely anything at all. Even if at times less penetrable paper should accidentally be placed in the filter, this, from the attention on the part of the workman, cannot easily cause an overflow of the paraffine, while the greater or lesser penetrability of the paper is easily observable during the first half hour by the regulation of the inflowing stop-cock, and this must be considered by the workman. 3. The whole apparatus is heated by waste steam. 4. The mixing and filtering apparatus occupy little room, and, *e. g.*, 25 hundred-weight of paraffine can be easily mixed and filtered in twenty-four hours.

In Figs. 44 and 45 are illustrated: A. The mixing apparatus. B. The filtering apparatus. The steam first enters the filtering apparatus, and then passes through the mixing apparatus into the open air.

The mixing apparatus A consists of a wrought-iron chest, with a turned cast-iron flange, covered with iron cement, in which are three openings for the admission of three cast-iron mixing-kettles. These kettles are fastened to the flange of the steam-chest by a few screws, in order to prevent any displacement which an insecurity of the discharging vessel would cause. The kettles, with the steam-chest, are rendered steam-tight (der dampfdichte Abschluss des Kessels) in the simplest manner by a band of rubber placed beneath the rim of the kettle.

About 75^{mm} above the deepest parts of the bottom of the kettle is cast a support 25^{mm} wide, of such a length that it, with its forward end provided with screws, projects through the tin face-plate of the steam-chest, perhaps 25^{mm} wide. At this point about 3^{mm} thickness of tin is strengthened by a disk fastened by sunken rivets and of 15^{mm} thickness, and provided with four bolt-holes for the reception of screw-tacks. From the outside a flange is tacked upon the end of the kettle support that is provided with screws, and by underlaying with hacked hemp and intimately mixed red-lead cement against the solidly-built face of the steam-chest is so placed that the four screw-holes in the flange correspond exactly with those of the opposite inner disk. After this flange is firmly drawn the end of the kettle support, which is plainly turned off or polished, shall project over the flange 2 to 3^{mm}. Now, four screw-tacks, which are supported by a six-angled truss, are brought into four screw-holes, which are at hand to receive the same, and drawn firmly and steam-proof against the outer flange, and each kettle support is provided with a 25^{mm} wide cast-iron stop-cock. In the distribution of crude paraffine, and, above all, where prepared paraffine is to be filtered, this invention applies equally well, as it completely soaks through several layers of uniform unsized paper by the avoidance of all cements.

It is recommended to provide the surfaces turned upon the lathe with fine circular grooves. In the lower portions of the steam-chests lie six pieces of thinly-drawn crude copper plates (without soldered edges) which are contrived after the manner of the tubes of locomotive boilers, and are so joined outside of the chest by cast-iron knees that they form a long pipe or hose, heated by steam, in which the air to be used for the mixing of the charcoal and paraffine is heated. The exit of this pipe stands diagonally over the mixing boiler in combination with a running tube or siphon, which, through the middle of the boiler, reaches almost to the bottom of the same, being sent off from the copper pipe through a stop-cock in diminished size. It is self-evident that the main pipe for the warmed air from the steam-boiler is to be protected from cooling.

The filter apparatus B consists first of two polished chests, partially within each other, with a common front wall. The latter also will not be touched by the steam, and this arrangement will rest or touch entirely upon the ground, in order, on this side, where the workman is busy for the most of the time, not to have a too strongly heated surface, and to make the real filtering apparatus as comfortably accessible as possible. Otherwise, were there here a double wall filled with steam, then certainly this must be protected from a too strong radiation of heat by a strong wall built in front 120^{mm} thick, and this would detract from the service of the filtering apparatus. Beside, the

a Litchford and Nation's patent, No. 890, 1872. *b* Hodges' patent, No. 3241, 1871.

arrangement chosen insures a cheaper and simpler construction. Then the greater extent of surface can be made impermeable to melted and heated paraffine only with the most extraordinary difficulty (and perhaps not at all); but all loss of paraffine by incompactness or insecurity is to be particularly avoided, so the inner filtering chest to serve for the reception of paraffine must be made of cast-iron in one piece.

The attachment of the steam-jacket is simple and plainly shown in the drawing. The bottom of the cast-iron filtering chest is inclined toward the front, and at the same time from both sides toward the middle; at the deepest point there is an exit tube, with stop-cock for the drainage of the prepared paraffine. In the interior the filtering chest has a projecting brim of perhaps 50^{mms} breadth, which on the rear wall, and at the same time on both sides, serves for the formation of steam space. Upon this edge rest 8 pieces of wrought-iron filter supports, each of which is capable of receiving two glass filters; thus there are 16 filters arranged in rows always in operation. The funnels are made of glass, because it more easily preserves the absolutely necessary cleanliness than if they were made of white tin. One need not fear the destruction of the glass if there is the proper amount of foresight shown on the part of the workman. In about twelve years there were scarcely one or two broken by me. In the midst of the filtering chest, along its length and 50 to 60^{mm} above the glass funnels of the paraffine-distributing pipe, there is a pipe 40^{mm} wide, closed at both ends, communicating through three supports with the corresponding terminal stop-cocks of the mixing kettles, and connected to both sides with eight small cast-iron stop-cocks of 4^{mm} width attached to a wrought-iron pipe. The small stop-cocks are screwed on, and for this purpose small pieces of wrought-iron have been placed with hard solder in the proper places on the distributing pipe.

The mouths of the small stop-cocks do not lie perpendicularly over the middle of the filter, but are nearly in the middle of a side, in order to prevent the perforation of the filter-point by droppings. The paper used for filtering is a thin, but tolerably firm, unsized pressed paper; it is broken after the manner of bent filters. A sheet 45 by 37^{mm} (one 40 by 40^{mm} would be more convenient) makes a filter that will serve comfortably for the filtration of about a hundred-weight of paraffine.

When working day and night I have always had the filters renewed after using twelve hours. The very little paraffine that remains in the paper is recovered.

It is recommended to surround the warm, radiating surface of the mixing and filtering apparatus with a simple and appropriate non-conductor. This is attained by inclosing the apparatus, and only the front wall of the filter chest is provided with a wooden jacket for securing an isolated stratum of air.

The covering of the apparatus is not shown in the illustration, in order not to interfere with its clearness; likewise the conveyance of the water which falls down from the steam in both apparatus (and which forms in the best of steam spaces) is not noted, since their position depends entirely upon local surroundings.

Finally, a word concerning the restoration of fresh bone-black and the treatment of that which has been used. It is known that the fresher charcoal is the more energetically it acts. In very large paraffine factories it is used on this account to prepare it from the coal itself, and by use it settles.

Comparatively speaking, very little can be restored with profit, as it is used even in the largest paraffine factories. In a business of less extent one will easily see from this that it is at least unprofitable to buy the powdered preparation of coal from the charcoal factories, because one receives with it in most cases smut and dust from the sifted granulated charcoal, and has not the slightest guarantee for the quality and freshness of the preparation. I have always, on this account, secured from a neighboring charcoal factory the small quantity of 100 kilograms of freshly prepared granulated and dust-free charcoal and allowed the pieces of coal to be immediately reduced to a fine powder for use in a simply constructed pulverizing cylinder (in Figs. 46 and 47). If one has not a charcoal factory in the immediate vicinity, and has not the certainty of obtaining the granulated coal entirely fresh at all times, then it is well worth the while to buy the pieces of coal in larger quantities and to allow the same to be thoroughly heated in kettles again, previous to the use of the coal which has been just pulverized.

The pulverizing cylinder (Figs. 46 and 47) is made of cast-iron (750^{mm} long and 500^{mm} in diameter) and revolves with riveted wrought-iron pegs in corresponding metallic holes in the facing; in the surface of the jacket or cover there is an opening for filling and emptying made close with gum. The cylinder is revolved best in slow revolutions (at most but two turns per minute). Within the cylinder there lies another massive cast-iron cylinder 120^{mm} in diameter, with a length equal to that of the drum. In twelve hours an apparatus of this size will pulverize perhaps 25 kilograms in the finest manner. These dimensions can be considerably increased without disadvantage.

The bone-black I have mostly used in quantity, not over 3 per cent. of the weight, and the paraffine retained by the same amounts to about the same weight. This silt from the powdered coal and paraffine is first heated together in a thick-walled kettle with return steam, whereby a greater part of the paraffine is separated into a clear liquid, which is scooped up with a shallow ladle and placed directly upon the filter paper.

The silt which has become thin is put in a large iron kettle, in which it, with the least quantity of water (from six to eight parts), is thoroughly cooked out over an open fire and under an active stream of steam, which is used from time to time. By the cooling of the mass almost all of the paraffine separates upon the top of the water as a firm but gray-colored layer, which is taken off, melted, and filtered through the paper with the other materials. A repeated boiling of the silt is seldom necessary, and this second operation almost never pays, because of the cost of the fuel in obtaining the paraffine. The powdered coal still so obstinately retains a very small percentage of the paraffine that this must be driven off by heating the coal, if the latter is to be again used as a decolorizer, or even if it is to be useful in the manufacture of acid phosphate of lime—superphosphate.

With this view I cause it to be thoroughly heated in an inclined cast-iron retort of about 2^{m} to 3^{m} long and 800^{mm} wide, and cross-cut almost elliptically, which is provided with an appropriate receiver for the condensation of the paraffine vapor. (This vapor never remains even at the lowest possible melting point of paraffine undecomposed, but yields paraffine of a low-melting point and oil as the product of decomposition). The paraffine that has been boiled out in shallow wrought-iron chests of perhaps 12^{mm} height and 1^{m} length, whose bottom conforms to the form of the retort, and both of whose sides have small and appropriate stop-cocks, is passed into the retort, and after the ensuing evaporation of all the paraffine (which is instantly known by the cooling of the discharge pipe of the retort) during the heating is left therein four to six hours long for the partial cooling.

Then the cast-iron chests, of which two are placed behind each other in the retort, are taken out and immediately covered with an appropriate tin cover, which is everywhere made close by a covering of clay, and the heated coal-dust is left standing therein until it has become perfectly cooled.

The taking out of the retort, the putting on and sealing of the cover, must take place as quickly as possible, in order to prevent the partial reduction of the coal to ashes. (*a*)

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a Dingler, ccxvi, 244.

Powdered fuller's-earth, marl, clay, or any similar substance, mixed with melted paraffine and allowed to subside, will deprive it of color, and the paraffine adhering to the subsided particles may be separated by heating with steam and agitation. (*a*) The successful use of these natural, insoluble silicates led to experiments upon the use of artificial silicates of the alkaline earths. For this purpose silicate of magnesia was found to answer all requirements best. This material is formed by the reaction of solutions of sulphate of magnesia and silicate of soda, the resulting silicate of magnesia being thoroughly washed and dried by steam heat. It is then added to the melted paraffine, and after it has subsided and the paraffine has been drawn off the residue is treated with dilute sulphuric acid. When the paraffine separates and rises to the surface the silica is precipitated, and the solution of sulphate of magnesia lies between them. The paraffine is removed, the solution of sulphate of magnesia is washed from the silica, and the silica is dissolved in caustic soda. It will thus be seen that the material is continually renewed with the addition of sulphuric acid and caustic soda. (*b*) It is found in using these silicates, whether natural or artificial, that a red heat destroys their action, and also that they must be used at such a temperature that the water of hydration is expelled, the coloring matter apparently taking its place. Hence, if the silicate is applied at a temperature only a few degrees above the melting point of the paraffine, it will have no action upon it until the temperature has been raised above that sufficient to expel the water. (*c*)

Another method which has been suggested for the removal of the oils from the soft paraffines consists in melting them with from 5 to 10 per cent. of oleine and cooling and pressing. Paraffine is insoluble in oleine. The mineral oils dissolved in oleine are separated from it by distillation, the former distilling at 220° C. and the latter at 280° C. (*d*) Bisulphide of carbon has also been used for this purpose. (*e*)

Although great efforts are made by all manufacturers of paraffine to prepare the wax of a beautiful pearly whiteness, it is a well-known fact, particularly among the manufacturers of continental Europe, that this freedom from color is not permanent for a long period. It is probable that paraffine obtained through the careful distillation of petroleum is purer and less liable to change than that made from distillation of shale or brown coal. Paraffine is often colored for candles and other purposes. As the beautiful colors produced from aniline are insoluble in paraffine, they are first dissolved in stearine, and the stearine is then melted into the paraffine; the color can be recovered, however, by melting the mixture and passing it through a filter. Two per cent. of stearine will give a clear pink color, and 5 per cent. a full crimson. Blue may be obtained with indigo, red with logwood, green with the two mixed and also with indigo and saffron, orange with logwood and saffron, and yellow with saffron. These colors may be readily incorporated with the mass by grinding a small piece of the paraffine with the color and then working it into the mass while hot. (*f*) To color paraffine black it is recommended that the wax be digested with the fruit of the *Anacardium orientale*, which contains a black fluid vegetable fat that combines with the paraffine and does not injure its illuminating properties.

SECTION 4.—PROPERTIES OF PARAFFINE.

Crude fossil paraffine from Galicia is brown, greenish, or yellow, translucent at the angles, with a resinous fracture. It is usually brittle, and when softened can be kneaded like wax, becoming dark on exposure to air. It becomes negatively electric and exhales an aromatic odor with friction. It melts at 66° C. (149° F.), but its illuminating power is such that 754 ozokerite candles equal 891 of ordinary paraffine, or 1,150 of wax. In 1871 Mr. John Galletly examined a paraffine from Boghead coal which melted at 80° C. and had a boiling point near the red heat, and which therefore presented great difficulties in the way of determining its vapor density. Distillation appeared to convert about half of it into liquid hydrocarbons, but the portion that remained solid after crystallization from naphtha retained its melting point unaltered. This specimen followed the general rule that paraffines from different sources diminish in solubility as the temperature increases at which they melt. The following illustrates this point:

Melting point.	Solubility in 100 c. c. of benzole at 18° C.
Deg. C.	*Grams.*
35.0	133.0
49.6	6.0
52.8	4.7
65.5	1.4
80.0	0.1

a Fordred, Lamb & Sterry's patent, No. 610, 1868.
b Smith & Field's patent.
c Frederick Field: *On the Paraffine Industry*, J. S. A., xxii, 349; Am. Chem., v, 169.
d P. Wagerman, Poly. C. Bl., 1859, 75.
e E. Allan, Dingler, cxlviii, 317; Poly. C. Bl., 1858, 1033.
f Eng. Mech., xxiii, 259.

Although only one part of the paraffine melting at 80°, dissolved in 1,000 of benzole at 18° C., it mixes with it in all proportions above its melting point. The densities of paraffines appear to increase with their melting points, but with specimens having the same melting points it is somewhat difficult to obtain the same results.

The following are numbers obtained with paraffines from Boghead coal: (*a*)

Melting point.	Specific gravity.
Deg. C.	
32.0	0.8236
39.0	0.8480
40.5	0.8520
53.3	0.9110
53.3	0.9090
58.0	0.9243
59.0	0.9248
80.0	0.9400

In 1878 E. Sauerlandt examined the relation of the melting point to the specific gravity of paraffines from ozokerite with the following results: (*b*)

Melting point.	Specific gravity.
Deg. C.	
56	0.912
61	0.922
67	0.927
72	0.936
76	0.939
82	0.943

Sauerlandt separated his paraffines by using solvents.

Sulphuric acid attacks all the paraffines, provided the temperature is sufficiently high. It is further observed that this acid more readily attacks the paraffines with high boiling points than those the boiling points of which are lower. The carbon separated from the paraffine melting at 80° C. by the action of sulphuric acid is in so fine a state of division as to pass through filter paper. Chlorine and nitric acid both produce substitution compounds with many specimens of paraffine, but the products are by no means uniform. (*c*)

It is not an infrequent occurrence to find samples of paraffine mixed with stearic acid and stearic acid containing paraffine. As these mixtures are made legitimately, and also for purposes of adulteration, it therefore becomes necessary to determine their constituents. Any attempt to determine the constituents of such a mixture by determining the density would of course be futile, as the density of neither paraffine nor stearic acid is constant. R. Wagner has proposed the following method, which may be used either qualitatively or quantitatively: Not less than 5 grams of the mixture are taken and treated with a warm solution of hydrate of potash, which must not be too concentrated. A soap is formed with the stearic acid, while the paraffine remains unaltered. Salt is then added until the soap separates as a soda soap and takes down the paraffine with it. The soap is thrown on a filter and is washed with cold water or very dilute ethylic alcohol. The salt is first washed out, and then the soap, finally leaving the paraffine on the filter, which is dried at a temperature below 35° C., care being taken not to fuse it. The paraffine is then carefully dissolved from the filter with ether by repeated washings and the solution carefully evaporated in a weighed porcelain crucible in the water-bath at a low temperature. The residue, consisting of paraffine, is then weighed, and the stearic acid estimated by difference. (*d*)

E. Donath saponifies the mixture with potassa and precipitates with calcium chloride. The calcium soap is washed on a filter with hot water and dried at 100° C. Part of it, after powdering, is extracted with petroleum ether, the extract evaporated at 100° and weighed, when the residue represents the paraffine. (*e*)

The most approved method of determining the melting point of paraffine consists in throwing a chip of paraffine on hot water and allowing it to melt. Then the water is slowly cooled, and the temperature is noted at which the globule of paraffine loses its transparency.

It has been found impossible in the amount of time that I have been able to devote to this portion of the subject to call attention to all of the great number of specific investigations that have been made upon paraffine, and the difficulty of attempting an exhaustive discussion of the subject is increased by the obscurity of the nomenclature. Paraffine in the United States and in the languages of continental Europe is used to signify the solid hydrocarbons obtained in distillates made at low temperatures, but in England the word has been given a

a *Chemical News*, xxiv, 187.
b *Hübner's Zeitschrift*, 1878, 81; Dingler, ccxxxi, 383.
c *Chemical News*, xxiv, 187.
d *Ibid.*, xxvii, 16.
e Dingler, ccviii, No. 2, *Am. Chem.*, iv, 196.

much wider signification, it having been applied to all of the fluid products of such distillation belonging to the marsh-gas series (C_nH_{2n+2}). It appears to me probable, however, that among the solid products to which this name is applied there are to be found the higher members of the series C_nH_{2n}, as well as the series C_nH_{2n+2}, the original substance to which Reichenbach gave this name belonging to the latter series. Among other facts which lend strong support to this opinion is the readiness with which some of the paraffines are attacked by reagents, forming substitution compounds, while others are, true to their name, nearly destitute of affinity. A. G. Pouchet acted on paraffine with fuming nitric acid and obtained an acid which he called paraffinic acid. Analysis of this acid, and also of its salts, showed its composition to be $C_{24}H_{48}O_2$, which indicated that the paraffine had a composition $C_{24}H_{50}$. (*a*) The proof seems equally convincing that the paraffine melting at 80° C. examined by Galletly belonged to the series C_nH_{2n}. It is therefore to be concluded that the opinion advanced as long ago as 1856 by Philipuzzi, that commercial paraffine may be separated into a number of bodies differing in boiling points, is correct, and that definite knowledge regarding the constitution of paraffines from different sources awaits further investigation.

CHAPTER V.—SUBJECTS OF INTEREST IN CONNECTION WITH THE TECHNOLOGY OF PETROLEUM.

SECTION 1.—"CRACKING."

The importance of that reaction which has been technically termed "cracking" scarcely admits of exaggeration. To assert that it is essentially destructive distillation, and that the results of its action are oils of decreased density, the decrease dependent upon the extent to which it obtains action, explains neither the nature of the reaction nor the importance of its effects. In the elaborate report upon petroleum made by Dr. J. Lawrence Smith to the judges of the Centennial Exposition he claims that the phenomena attending the destructive distillation of petroleum were first observed by Professor B. Silliman, jr., and noted by him in his famous report of 1855. (*b*) Professor Silliman says:

> The uncertainty of the boiling points indicates that the products obtained at the temperatures named above were still mixtures of others, and the question forces itself upon us whether these several oils are to be regarded as *educts* (*i. e.*, bodies previously existing and simply separated by the process of distillation), or whether they are not rather produced by the heat and chemical change in the process of distillation. The continued application of an elevated temperature alone is sufficient to effect changes in the constitution of many organic products evolving new bodies not before existing in the original substance.

When consideration is had of the knowledge possessed by chemists concerning petroleum and similar substances at the time Professor Silliman made this unique and original investigation the above paragraph is properly regarded as remarkably sagacious and suggestive. No one in 1855 knew whether native petroleum was a homogeneous fluid decomposed by distillation, as are fixed oils, or a mixture of a great number of fluids separated by distillation, as it really is. Professor Silliman's question remained unanswered until Pelouze and Cahours, and later Warren and Storer, attempted to ascertain what manner of substance petroleum really is. Warren and Storer published their results in 1865, (*c*) and showed that they had succeeded in isolating, in a state of purity, portions of the members of three homologous series of hydrocarbons. Two of these series were isomeric, but the boiling points of the corresponding members of the two groups were about 8° C. apart. Professor J. D. Dana has regarded these hydrocarbons as educts, and has placed them in his system of mineralogy in their proper place as natural, not artificial substances. The fact that they have been isolated in such a degree of purity that considerable quantities have been obtained having a constant boiling point, a constant chemical composition, and furnishing accurate results on the determination of their vapor densities, furnishes all the testimony that chemists can reasonably ask regarding the question whether they are educts or products. The analogy found to obtain between these constituents of petroleum and those of the distillates from albertite, Boghead mineral, cannel coal, and lime soap made from menhaden oil has been considered by some chemists to indicate that, whereas the constituents of these distillates are the constituents of products of destructive distillation, petroleum must be destructively distilled in order to furnish them. Might not these unquestioned facts be so interpreted as to regard petroleum itself as a product of destructive distillation, and the similarity of these fractional distillates be also regarded as an additional proof that all of these products of a similar process, acting on similar materials, are very complex mixtures of compounds

a C. R., lxxix, 320; J. C. S., xxviii, 50. *b* Am. Chem., ii, 18. *c* Mem. A. A. (N. S.), ix, 135; see also page 54.

of carbon and hydrogen that are related to the petroleum as *educts*, and not as *products?* I think all of the phenomena connected with this subject are most satisfactorily explained upon this hypothesis.

I quote the following paragraph from the paper read by A. Bourgougnon at the meeting of the American Chemical Society, held September 7, 1876: (*a*)

During the distillation the products are more and more heavy until the heat produced decomposes the oil in the still; then the oil is dissociated, and by this dissociation, or "cracking", lighter and also more inflammable products are obtained. At the same time this decomposition is accompanied by a formation of carbon, which is deposited in the still, and gases of a very offensive odor pass off with the oil.

This is the first instance that has come under my notice in which this very proper term (*dissociation*) is applied to this reaction. The phenomena of dissociation are constantly observed throughout the entire range of technical and scientific operations. Even marsh-gas, by a sufficiently high temperature, is resolved into hydrogen and the carbon of the gas retorts; the coal is resolved by dissociation, at a red heat, mainly into marsh-gas, coal-tar, and coke; at a less elevated temperature into those hydrocarbons homologous with marsh-gas, ranging through all of the paraffine series from marsh-gas to solid paraffine wax, leaving a residue of coke. At the temperature required for this last operation a small percentage of another series of hydrocarbons homologous with ethylene appears, but none of the benzole series that characterize coal-tar. "It has been observed that the schistoils of Buxière-la-grue and of Cordesn do not contain benzole and naphthaline, because the distiller purposely works at too low a temperature". (*b*)

Antisell, in *Photogenic Oils*, page 45, says:

The tendency of destructive distillation is to produce compounds possessing more simplicity of composition than the original substance, and capable of sustaining the higher temperatures at which they form unaltered; so that, under the range of temperature indicated (300° to 2732° F.), liquids will be formed when the temperature is least, as at the commencement, and gases when the heat has arisen to the high point set down; and as in the lower ranges, where liquids are produced, the effect of this augmented heat within this lower range is to lessen the complexity of the compound by dropping or reducing its amount of carbon or of hydrogen, it is at the very lowest temperatures that the liquids containing the highest number of atoms of carbon and hydrogen will be found; and when the temperature arises to that essential to the formation of gas, this gas (a carbide of hydrogen) is produced at the expense of the complex liquids formed at first, which give off some carbide of hydrogen, and thus have their proportions simplified.

If then, as has been assumed in these pages, petroleum is the product of the destructive distillation of pyroschists at the lowest temperature possible, it naturally follows that the paraffine series, from marsh-gas up to solid paraffine, would form the bulk of the educts of petroleum. This opinion is confirmed by all that is known either by technologists or chemists concerning the proximate principles that are the *normal constituents of the Paleozoic petroleums found on the western slope of the Alleghanies;* and it is doubtless to this fact that they owe in large part their great superiority over the petroleums of other localities, because the paraffine series of compounds contain the largest proportion of hydrogen as compared with the carbon of any series known to chemists.

Now, when these compounds of the paraffine group are subjected to temperatures above their boiling points, they are dissociated, and the researches of Thorpe and Young upon the distillates of paraffine wax under pressure have shown that they are not decomposed into the lower members of the same series, but into the olefine series, the proportion of the paraffine series being comparatively small. The significance of this discovery lies in the fact that the olefines contain less hydrogen in proportion to the carbon than the paraffine group, and in combustion produce a less brilliant and luminous flame; hence it is to be inferred that while "cracking" will convert a large percentage of petroleum into illuminating oil, the oil will be inferior in quality just in proportion as it consists of cracked oils. The statement that has been made that the present process of manufacture "takes the heart out of the petroleum" for high test-oils and leaves an inferior residue for the ordinary 110° oil is not without some foundation in fact; but it is not true as a general statement, for the amount of material existing in ordinary petroleum suitable for the production of high test-oil is estimated at 10 per cent., while the whole amount of illuminating oil is about 70 per cent. Manifestly, then, the manipulation of the petroleum is a matter of great importance to the consumer of these oils. The manufacturers of reduced petroleum and of high test-oils prepare a strictly paraffine oil from the educts of the petroleum, and convert the remainder either into an 110° oil by "cracking" or into paraffine oils and wax by careful fractional condensation. The 110° oil produced by cracking alone would be much inferior to the same grade of oil produced in an establishment where the bulk of the petroleum was converted into an oil that consists of both educts and products of the distillation.

Illuminating oils are classed and sold as "Water White", "Standard," and "Prime", according to their color. The oils belonging to the paraffine series are neutral, inert oils, not readily acted upon by chemical reagents, and not readily forming substitution compounds. Sulphuric acid removes from such oils the small percentage of unstable oils which they contain and leaves them colorless and limpid or "Water White". With the standard and prime oils, consisting largely of "cracked" oils, the case is wholly different, as they contain members of the olefine group which form substitution compounds with sulphuric acid with great readiness. These compounds are not readily destroyed by solutions of caustic alkali, and therefore remain in the oil. These oils blacken when heated to 200° F., and discharge sulphurous acid (SO_2). When burned, they cause the wick to coat and discharge

a Am. Chem., vii, 81. *b Chemical News*, xxviii, 22.

sulphurous acid with the products of combustion. This is abundantly demonstrated by the researches of the German chemist, J. Biel, (*a*) in which he compared oils manufactured from Russian and American petroleum with results shown in the following table:

Varities examined.	Specific gravity at 16° C.	Tension of vapor at 35° C.	Flashing point.	Inflaming point.	Essence or naphtha.	Burning oil.	Heavy oil.	THE COMPARATIVE ILLUMINATING POWER AT—			
								6cm.	9cm.	12cm.	14cm.
		Millimeters.	*Deg. C.*	*Deg. C.*	*Per cent.*	*Per cent.*	*Per cent.*				
Standard	0.795	160	26	30	14.40	45.90	39.7	7	3.35	1.36	0.80
Astral	0.783	5	48	51	2.20	87.80	10.0	7	4.50	3.00	1.36
Imperial	0.789	13	44	46	5.50	80.00	14.0	7	6.00	3.00	1.36
Russian O	0.803	201	26	29	33.50	66.50	....	7	6.25	4.45	3.70
Russian A	0.817	73	28	30	15.40	73.20	10.5	7	5.20	4.00	3.00
Russian B	0.822	45	30	35	12.80	78.30	8.4	7	5.70	3.20	1.65
Russian C	0.821	95	25	26	15.25	71.25	13.5	7	....	....	....

I presume the Imperial oil is an oil manufactured in Germany from crude American petroleum. A comparison of these results shows the great superiority of the Astral and Imperial oils over the Standard. (*b*)

Because these oils, cracked by one distillation and necessarily imperfectly cracked and finished by treatment, are of inferior quality, it is not, however, to be concluded that cracked oils cannot be made of superior grade. The earliest practical application of destructive distillation to the manufacture of illuminating oil was made by the late Luther Atwood, of Boston, Massachusetts. He patented the product and apparatus for obtaining it in 1859, and the process was placed in operation by Mr. Joshua Merrill, of the Downer Kerosene Oil Company, before petroleum became an article of commerce. Mr. Merrill treated thousands of barrels of heavy oil, purchased from those who could not work them often at as low a price as 10 cents a gallon, and cracked them into burning oil of 45°, which, at that time, was readily sold at from 90 cents to $1 40 per gallon. The Downer company have worked this process ever since and have made more or less cracked oil, but they work at low temperatures with steam, and have never made their burning oil with one distillation. Their oils are highly finished products, and the very high reputation that they have always borne is a sufficient guarantee of their excellence. There is really upon the market a great variety of illuminating oils prepared from petroleum, some of which at double the price are cheaper than others, without regard to either their appearance or their safety.

An experiment was made in Boston some years since, which, while without results of practical value, confirmed the views stated above. It was assumed that by cracking naphtha permanent gases would be obtained, and the attempt was made to convert the naphtha into a mixture of marsh-gas and hydrogen by injecting steam into a vessel filled with the volatile liquid. The result was so far successful as to produce a considerable amount of permanent gases, and on evaporating the naphtha remaining a residue of heavy lubricating oil was obtained. (*c*)

Paraffine oil has been frequently converted into illuminating gas by allowing it to drip upon red-hot coke and by other similar processes. An analysis of such a gas in one instance showed it to consist of—

	Per cent.
CH_4, marsh-gas	54.92
C_2H_4, ethylene	28.91
H, hydrogen	5.65
CO, carbonic oxide	8.94
CO_2, carbonic acid	0.82

The presence of ethylene in such large proportion with free hydrogen indicates that at a lower temperature the homologues of that gas would probably be found in still larger proportion. (*d*)

SECTION 2.—"TREATMENT."

Next to the distillation of oils no question is of more importance than the chemical treatment which the distillates receive. It has always been claimed by the Downer company that the proper treatment for illuminating oil is washing with oil of vitriol, to which is sometimes added bichromate of potash, from which the sulphuric acid sets free chromic acid, and then washing with solution of caustic soda, and, finally, distillation over caustic soda. This treatment at one time produced oils that were unrivaled in the markets of the United States, and they have always held a very high reputation. It is, however, claimed by manufacturers of equally high

a Dingler, ccxxxii, 354; Indus. Z., 1879, p. 204; Chem. Z., 1879, p. 285.

b This is a general trade-mark, and not the exclusive property of the Standard Oil Company.

c S. Dana Hayes, A. J. S. (3), ii, 184. I accept the conclusions reached by Mr. Hayes; but the experiment was not conducted so as to exclude the possibility that the heavy oils were dissolved in small quantity in the several thousand gallons of crude naphtha used.

d Archiv der Pharmacie, June, 1874; Am. Chem., v, 431.

reputation that the finishing of oils by distillation is wholly unnecessary, if not positively detrimental. Judging from all that I can learn in reference to this subject, I conclude that the treatment that distillates should receive depends upon what they are. There are:

1. Distillates produced by reducing petroleum.
2. Distillates taken off before cracking commences.
3. Distillates that are wholly cracked.
4. Distillates that are mixtures of 2 and 3.

The first and second classes would consist almost wholly of the paraffine series (C_nH_{2n+2}) of hydrocarbons; that is, inert and neutral to chemicals. Consequently they would be easily treated, and would yield colorless and neutral oils, especially when more or less caustic ammonia is used along with or after the soda treatment. Classes three and four, however, are quite different. These consist of more or less of the olefines (C_nH_{2n}) that are not chemically inert, but form substitution compounds with readiness with such an active reagent as oil of vitriol. In these substitution compounds SO_2 takes the place of two atoms of hydrogen in the hydrocarbon, and the hydrogen unites with the atom of oxygen to form water. It is claimed by those who finish oil by distillation that these substitution compounds are not destroyed by agitation with caustic alkali. Others admit that they are not destroyed by caustic soda, but claim that they are removed by caustic ammonia. I am inclined to think that neither of the caustic alkalies will remove them. I have examined a large number of illuminating oils during the last twenty years, and I have found that a large proportion of them blacken on being heated to 200° F. and yield sulphurous acid fumes. I have never attempted to estimate this quantitatively, but the amount yielded by half a pint has in several instances been such as to be very apparent in the atmosphere about the apparatus. Such oils have not been properly treated. Half a pint is no unusual amount to consume on a winter's evening, and while in the experiments to which I have referred the sulphurous acid was disengaged suddenly and almost instantaneously, the fact that when the oil was burned it would be thrown off slowly would not lessen its quantity nor its effect upon those exposed to its influence. My own conviction is that all oils that will blacken and give off sulphurous acid should be finished by distillation over caustic soda.

The following abstract of an elaborate research undertaken by royal command, and published in Dingler's *Polytechnic Journal* and many other German scientific periodicals, has not before been translated so far as I have learned. Its importance demands for it a wider circulation. The author, H. Vohl, appears to use the term "Roh-petroleum" to designate American refined oils imported into Germany. He asks "if by the burning of petroleum there is not danger of producing unhealthful gases, and whether crude (Roh) petroleum does not itself contain injurious compounds which are kindled by its burning that are removed when it is purified?" and then continues:

The only element of crude petroleum which liberates unwholesome gases when it is burned is sulphur. No petroleum is free from it. In many cases the petroleum is polluted, in the so-called "cold treatment" with sulphuric acid, by sulphur compounds. It is particularly so when an appreciable quantity of paraffine is left in lamp oil, and because of its dark color is subjected to an additional treatment of sulphuric acid. In this way refined oil often contains or retains so much sulphuric acid that its burning develops unwholesome influences. Sulphuric acid in part forms a compound with the heavy paraffine oil which is soluble in the remaining oil, and neither through treatment by water nor by alkalies is it decomposed, so that a subsequent treatment with these substances offers no guarantee for the absence of sulphur. When oil so treated is subjected to distillation, first a clear burning oil passes over, then a rapid development of sulphurous acid gas, often accompanied with coloration of the contents of the retort. Finally, after a limited separation of sulphur has taken place in the neck of the retort, sulphureted hydrogen comes over, and a carbonaceous mass with acid reaction remains. An erroneous opinion is held in many places that a strong blue reflection possessed by many kinds of petroleum is an indication of its superior quality and usefulness Petroleum has this peculiarity when it contains an appreciable quantity of paraffine oil. Most hydrocarbons resembling retinols have these blue reflections, with a high melting point. None of the different kinds of petroleum investigated were free from sulphur or sulphuric acid, and therefore it can be assumed with justice that petroleum burning-oil free from sulphur belongs to the exceptions.

Petroleum, wherever a tranquil light is necessary, has superseded illuminating gas; besides, it is cheaper than coal-gas, so that it is entirely out of the question that the consumption of petroleum should decrease to any important extent, and therefore so much the more necessary in order to direct attention to these sulphur contents, that the removal of the injurious contents must be provided for. Among those who make use of petroleum for illuminating purposes inflammation of the eyes and catarrhal troubles often appear, for which physicians can never afford relief, because the source of the trouble is unknown to them.

The series of experiments embraced the following determinations, beside the sulphuric acid:

(*a*) The specific gravity of the oil at 15° R. water =1.000.

(*b*) The temperature (R.) at which the oil gives off inflammable vapors.

(*c*) The contents in oils of specific gravity 0.740.

(*d*) The contents in paraffine oils of specific gravity, 0.850, solidifying at + 15° R.

(*e*) The consumption of the oil, in grams, per hour in a lamp with a plain burner, with a wick 18^{mm} broad and 2^{mm} thick, having a capillary attraction of 8^{cm}.

In order to determine whether the sulphur is contained as sulphuric acid or as a substitution compound of sulphuric acid with an hydrocarbon, he heated the oil a long time at the boiling point in a glass retort with a piece of sodium or potassium. The bright surface of the alkaline metal is soon covered by a yellowish layer, so that one can safely conclude upon a sulphureted compound in the oil. After cooling add distilled water drop by drop until the excess of alkaline metal becomes oxidized and the sulphur, as sulphide of potassium, passes into solution. Then stir the fluid with a glass rod that has been immersed in a solution of nitro-prusside of sodium. The presence of the smallest quantity of sulphur will immediately color the solution a beautiful violet-blue. (*a*)

a Dingler, ccxvi, 47; W. B., xxi, 1053.

TABULAR STATEMENT OF EXAMINATION OF OILS BY H. VOHL.

No.	Specific gravity.	Temperature at which inflammable vapors are given off.	Per cent. contained in oils of specific gravity 0.740.	Per cent. contained in oils of specific gravity 0.850.	Hourly consumption of oil in grams.	Per cent. of sulphuric acid contained.
		Deg. R.				
1	0.780	28.0	24.964	14.195	16.78	0.994
2	0.790	28.0	18.330	19.519	15.46	2.001
3	0.790	28.0	3.050	5.022	15.00	1.884
4	0.780	27.0	19.889	14.987	16.50	0.946
5	0.805	24.0	22.133	28.666	17.11	1.560
6	0.790	23.0	25.950	9.669	17.20	0.876
7	0.800	27.0	25.345	11.500	14.88	0.998
8	0.790	22.0	35.460	11.590	17.90	1.014
9	0.795	23.5	25.203	12.100	17.12	0.914
10	0.795	27.0	15.233	5.410	14.50	0.348
11	0.800	24.0	25.575	35.769	16.00	3.114
12	0.790	19.0	32.440	19.711	16.14	1.440
13	0.790	19.5	29.580	28.711	17.25	2.100
14	0.790	19.0	33.216	26.461	16.89	1.210
15	0.785	18.0	34.706	3.506	17.98	0.346
16	0.779	8.0	48.051	20.512	19.38	1.950
17	0.790	19.0	38.193	23.367	18.25	2.146
18	0.800	27.5	20.950	32.550	16.50	2.200
19	0.798	25.5	20.600	26.480	17.33	0.216
20	0.795	23.0	21.400	27.140	17.50	0.220
21	0.790	23.0	25.400	35.440	14.20	0.389
22	0.795	24.0	24.116	36.880	14.29	0.401
23	0.790	22.0	36.118	13.400	17.55	0.991
24	0.790	19.0	35.661	14.014	17.24	0.973
25	0.800	27.0	10.033	6.880	15.36	0.310
26	0.795	26.0	18.000	8.446	16.02	0.300
27	0.795	26.0	17.880	9.001	15.98	0.310
28	0.780	9.0	48.336	20.330	19.06	1.977

The amount of sulphur indicated by this table is surprisingly large, but I think it should have been computed as sulphur rather than as sulphuric acid. As sulphuric acid it is already oxidized and would not decompose at 200° F. and appear as sulphurous acid. It is compounds that will burn into sulphurous acid gas, and not sulphuric acid, that render these oils noxious. No examination that I have ever made has led me to think sulphuric acid (SO_3) is present in illuminating oil.

SECTION 3.—"SLUDGE."

"Sludge" is the name applied to the refuse acid and alkali solutions from the agitators. When petroleum first began to be extensively manufactured, many attempts were made to recover both the acid and the alkali from these spent solutions. The acid forms a black, tarry mass, and the alkali a sort of soapy curd, that forms flocks of a rusty color, and also compounds that pass into solution, as well as sulphate of soda. By evaporating the soda sludge to dryness and calcining to burn out the organic matter an impure carbonate of soda is obtained that can be converted into caustic soda by the ordinary process. The sulphate of soda and other impurities thus accumulate in the soda solution and finally render its action imperfect. As this simple process for recovering the soda has never been used to any considerable extent, I infer that it has never, on the whole, been considered profitable. There was used during the census year an amount of soda crystals, soda-ash, and caustic soda estimated to be equivalent to 3,500 tons of soda-ash, all of which ran to waste.

The sludge acid is recovered by first heating it, when it separates into an oily superficial layer and a heavy layer beneath containing the acid. This acid liquid is drawn off and evaporated and concentrated like chamber acid, the black carbonaceous matter being destroyed at the high temperature required for concentration. This process is also very simple, but it produces abundant suffocating fumes and disagreeable odors, and in the neighborhood of dense populations is justly considered a great nuisance. At Cleveland, Ohio, and near Titusville, Pennsylvania, there are establishments for recovering spent acid, to which the acid sludge is carried in tank-cars. The manufacturers of petroleum are paid an amount sufficient to induce them to put their sludge into tank-cars rather than to allow it to run to waste, and the recovered acid is returned to them at the ruling price for sulphuric acid. Sludge acid is sold to the manufacturers of commercial fertilizers in localities where the refineries are convenient to such establishments. Much, however, is allowed to run to waste; it is run into rivers and lakes, and, in the neighborhood of New York, is conveyed in barges outside of New York harbor and emptied into the sea. The amount of this material that has been thrown into Oil creek and the Allegheny river is enormous. It has lodged upon the rocks and on the gravel along the creek and stained them black; and it floats upon the river continually, often communicating its peculiar odor to the atmosphere above. I have also noticed it from the deck of a Sound steamer floating on the East river, its peculiar odor being perceptible at the level of the deck nearly all of the distance from Blackwell's island to the Battery. During the census year 45,819.5 tons of sulphuric acid were used in the manufacture of petroleum products. Of this vast quantity 21,158.75 tons were recovered, 22,162.5 tons were sold to manufacturers of fertilizers, and 2,498$\frac{1}{8}$ tons were "run to waste", which phrase means discharged into lake Erie, the tributaries of the Ohio river, the Delaware river, Chespeake bay, or the ocean.

The effect of both acid and alkaline sludge upon fish was investigated by Dr. Stevenson Macadam, and the results were communicated in 1866 to the British Association for the Advancement of Science. He made dilute solutions of different strengths and immersed fish in them with the following results:

1, a fish placed in the acid sludge died in five minutes; 2, in one part sludge and three of water, it died in ten minutes; 3, in one part sludge and twenty of water, it died in fifteen minutes; 4, in one part sludge and one hundred of water, it died in fifteen minutes; 5, in one part sludge and one thousand of water, it died in two hours; while in one part sludge to ten thousand parts of water the fish were not killed for twenty-four hours, but were apparently sick and prostrate. The spent-soda liquor which has been employed in treating oil which has been previously acted upon by acid is decidedly alkaline and caustic in its nature. It has extracted from the oil and holds in solution more or less carbolic acid and its homologues, and the poisonous nature of the spent-soda liquor is doubtless augmented by the presence of these acids. A sample of this soda liquor which was flowing from a paraffine oil manufactory, and which contained extra water, proved destructive to fish in ten minutes; with three parts of water it killed fish in twenty minutes; with twenty parts of water, the fish were dead in twenty-five minutes; with one hundred parts of water, the fish were dead in thirty minutes; diluted with one thousand times its volume of water, the soda liquor proved destructive to fish in twenty hours; while with ten thousand parts of water the fish were not killed, but were apparently slightly sick. (a)

He also found that shale oil, Pennsylvania petroleum, and their manufactured products, were all deleterious to fish; but the shale oil was more injurious than petroleum.

If these sludge solutions were mixed, and as a result sulphate of soda instead of free sulphuric acid and caustic soda were discharged into the streams, the injurious effects upon animal life would without doubt be lessened; but even in that case the discharge of such vast quantities of mineral and organic poisons into streams the waters of which are used by thousands of the inhabitants of the towns upon their banks cannot be viewed as anything less than a public misfortune, if no regard whatever is had to the fish with which the streams are stocked. The extent of such injury as a problem in public health, as compared with other interests, is properly a subject of inquiry for the physician.

SECTION 4.—FIRES.

The attention of the public was called to the great danger of allowing large quantities of either crude or refined oil to be stored within the limits of large cities by the disastrous fires that occurred in Philadelphia in March, 1865. A quantity of oil, amounting to what would now be considered only a few thousand barrels, was stored in some open sheds on a lot that was not otherwise occupied. This oil was set on fire, as was supposed by an incendiary, very early on a cold morning early in March. The flames spread rapidly, and as the barrels burst the contents accumulated in a pool of burning oil that soon overflowed the lot, and, filling the frozen gutters, ran down a narrow street in the neighborhood in a rivulet of flame as high as two-story houses. Houses were set on fire, and their occupants, fleeing for life, were overtaken by the stream of fire and burned before they could escape. In this way several lives were lost. This catastrophe led to the enactment of laws forbidding the storage of petroleum within the limits of large cities, and in the case of Philadelphia the railroad carried a branch track to tide-water below the city for its delivery and shipment.

Petroleum refineries have been considered especially liable to destruction by fire, yet some of the oldest establishments in the country have received very little injury from that source. The amount of capital invested in the manufacture of petroleum during the census year was $27,325,746. Of this, $21,196,246 was used twelve months, $318,000 eleven months, $2,315,000 ten months, $2,019,000 nine months, $727,000 eight months, $100,000 seven months, $510,000 six months, $100,000 five months, $36,000 four months, and $4,500 three months, equal to $25,781,327 used for twelve months. During the same time the losses from fire in the refineries of the country amounted to $104,631, or less than one-half of 1 per cent. When to this invested capital is added the total value of manufactured products that passed through these establishments, equal to $43,705,218, the total being $71,100,964, these losses are insignificant. The refineries lately constructed are for the most part uncovered, and the material about them that can burn is reduced to a minimum; but the older refineries that have not burned are inclosed in very substantial buildings, provided with ample means for completely filling them with steam in case of any accidental ignition of the oil. Really the danger from fire depends upon the want of care exercised by those who have charge of the refineries more than upon any especial appliances for preventing or extinguishing them. The great fire in Titusville in June, 1880, and caused by lightning. Against the occasional destruction of property by the elements no amount of foresight or precaution will prevail.

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a *Chemical News*, xiv, 110.

SECTION 5.—THE SPECIAL TECHNOLOGY OF CALIFORNIA PETROLEUM.

The earliest attempts to manufacture the petroleum of southern California were made by Mr. Gilbert, of San Buenaventura, about 1860, who distilled the malthas of the Ojai ranch and obtained from them a small quantity of oil of inferior quality that could be used for illumination. When I commenced my experiments in 1865 upon the same material I was soon convinced that it was quite different from the petroleum with which I was familiar on the Atlantic coast. The yield of oil of a specific gravity suitable for illuminating purposes was small in quantity, and burned in the lamps in use for Pennsylvania oils with a dull and smoky flame. The proportion of oil of medium specific gravity was very large, and the heavy oils, while of very low specific gravity, were not unctuous, and were destitute of lubricating properties. One of these denser distillates, with a specific gravity of 16° B., was a mobile fluid-like water or an essential oil. When the Hayward Petroleum Company and Stanford Brothers commenced the manufacture of petroleum from their springs and tunnels in San Francisco they encountered the same difficulties on a large scale. The oils were all of inferior quality, and the "middlings", as they were called, were so large a proportion of the distillate as to prove a very great obstacle to the success of the enterprise.

Professor Silliman secured a barrel of the Ojai malthas and carried it to Boston, where he worked it in the experimental apparatus of the Downer company. From the report of his results I make the following abstract:

The crude oil is very dark. At ordinary temperatures (60° F.) it is a thick, viscid liquid, resembling coal-tar, but with only a very slight odor, and with a density of 0.980 or 13½° B. It retains, mechanically entangled, a considerable quantity of water. The tar froths at the commencement of distillation from the escape of watery vapor. It yields by a primary distillation no product having a less density than 0.844, or 37° B. at 52° F. Distillation to dryness gave:

	Per cent.
Of oil having a density of 0.890 to 0.900	69.82
Coke, water, and loss	30.18
	100.00

This first distillate, having a density of about 0.890 at 60° F., gave, when subjected to slow distillation, a product having a density of 0.885, which, after treatment with oil of vitriol and soda lye and redistillation from soda, had a density of 0.880. This distillate was then fractionated, and yielded:

	Per cent.
Light oil of specific gravity 0.835 at 60° F	21.58
Heavy oil of specific gravity 0.880 at 66° F	37.41
Heavy oil of specific gravity 0.916 at 64° F	34.53
Coke	6.48
	100.00

In another experiment, undertaken with a view to "cracking", treating, and redistilling with soda, the products were expressed in percentages of the whole amount operated upon as follows:

	Per cent.
Naphtha of specific gravity 0.760 at 60° F	11.33
Oil of specific gravity 0.836 at 60° F	66.22
Oil of specific gravity 0.893 at 60° F	12.67
Oil of specific gravity 0.921 at 60° F	3.56
Loss	6.22
	100.00

Further experiments by distillation under pressure gave:

	Per cent.
Light oil, specific gravity 0.825 at 60° F	19.20
Heavy oil, specific gravity 0.885 at 60° F	25.86
Heavy oil, specific gravity 0.918 at 60° F	38.14
Coke and loss	16.80
	100.00

No paraffine could be detected by refrigerating any of these heavy oils in salt and ice. (*a*)

On returning from California to New England, in 1866, I brought with me a few gallons of several of the petroleums and malthas of the neighborhood of San Buenaventura. It was my intention to treat these samples in an apparatus similar to that used by Mr. Merrill, but the small quantity of each specimen at my disposal rendered that operation very difficult, and I subsequently determined to distill them under pressure, after the manner patented by Young. I contrived a small retort, with a valve of peculiar construction, described in the *American Journal of Science* for September, 1867. (*b*) These specimens of petroleum, numbered I, II, and III, were subjected to this treatment. No. I came from a tunnel in the Sulphur mountain (see Fig. 6), with a specific gravity 0.9023; No. II, from the Pico spring, with a specific gravity 0.8932; and No. III, from the Cañada Laga spring, with a specific gravity 0.9184. They were first subjected to distillation under a pressure of about 30 pounds per square inch in a

a A. J. S., xliii, 242; C. N., xvii, 257; B. S. C. P., 1868, 77. *b* A. J. S. (2), xliv, 230; C. N., xvi, 199; W. B., 1867, 725.

measured quantity of 1,500 c.c. The distillate obtained was then fractionated until the specific gravity of the distillate averaged 0.810 or 43° B. The heavy residue in the retort was again distilled under pressure and fractionated to a distillate of specific gravity 0.810. The heavy residue in the retort was then treated for lubricating oil. The results tabulated as follows:

1,500 c. c. of crude oil for each experiment.	First pressure distillation.	Coke and loss at distillation.	First fractionation of sp. gr. 43° B.	Heavy residue for re-distillation.	Yielding by second pressure distillation.	Second fractionation of sp. gr. 43° B.	Total crude illuminating oil.	Three per cent. loss in treating illuminating oil.	Total yield of refined oil.	Total crude lubricating oil.	Three per cent. loss in treating lubricating oil.	Total refined lubricating oil.	Yield of refined illuminating oil.	Yield of refined lubricating oil.	Loss in refining.	Loss in distillation.
Cubic centimeters:																
I	1,365	135	630.00	735.00	681.00	184.00	814.00	24.42	789.58	497.00	14.91	482.09	789.58	482.09	39.33	180.00
II	1,315	185	850.80	464.20	408.78	102.19	952.99	28.59	924.40	306.59	9.19	297.40	924.40	297.40	37.78	240.42
III	1,240	260	605.00	635.00	571.50	142.87	747.87	22.43	725.44	428.63	12.85	415.78	725.44	415.78	35.28	323.50
Percentages:																
I	91.00	9.00	42.00	49.00	45.40	12.27	54.27	1.63	52.64	33.13	0.99	32.14	52.64	32.14	2.62	12.00
II	87.66	12.34	56.72	30.94	27.25	6.81	63.53	1.91	61.62	20.44	0.61	19.83	61.62	19.83	2.52	16.03
III	82.66	17.34	40.33	42.33	38.10	9.52	49.85	1.40	48.36	28.58	0.86	27.72	48.36	27.72	2.35	21.57
Cubic centimeters:																
IV	1080.00	232.50	250.00	830.00	747.00	186.75	436.75	13.10	423.65	560.25	16.80	543.45	423.65	543.45	20.90	503.00
Percentages:																
IV	72.00	15.50	16.70	55.30	49.80	12.40	29.10	0.90	28.20	37.40	1.10	36.30	28.20	36.30	2.00	33.50

The specimen of maltha (IV) examined was taken, it is supposed, from the same pool on the Ojai ranch as that examined by Professor Silliman. Its specific gravity was 0.9906. The air, hydrogen sulphide, and water was removed by allowing the maltha to flow slowly from one vessel through a second vessel, in which it was heated sufficiently to expel these impurities, and from which it flowed into a receiver. The loss by this treatment was 12½ per cent. The purified maltha was then treated precisely like the oils, with the results as given above.

As these results, both with malthas and oils, were conducted on a small scale, the percentage of loss is much greater than would be experienced on a commercial scale.

A comparison of the results of the distillation of the malthas and oils appear at first sight to give the latter great preponderance in value over the former; but it should be borne in mind that the malthas contain 12½ per cent. of volatile impurity not contained in the oils. After making due allowance for this fact, it will be observed that the total amount of crude distillate is in all cases very nearly in the same proportion to the pure bitumen contained in the crude materials. These crude distillates yield easily to treatment with the ordinary amount of sulphuric acid and soda lye. The purified oil is very transparent and the most free from color of any that I have seen. Indeed, were it not for its opalescent properties, and the peculiar manner in which light is refracted by it, this oil could not be distinguished by the eye from pure water. I do not claim to have produced oils the burning qualities of which are superior to other California oils, but I think them in no way inferior to the best that have been produced from unadulterated California petroleum. The best refined California petroleum that I have made, as also the best that I have seen from other sources, fails to produce a light of such intense whiteness as the best refined Pennsylvania oils, although they are quite equal to the average upon the market. It is my opinion that this difference is due to admixture of some series of hydrocarbons, *containing a large amount of carbon in proportion to the hydrogen, in such quantity as to render the combustion incomplete, and thus give rise to a yellow flame.* (a)

An examination of Russian petroleum in 1881 by Kurbatow and Beilstein has shown the presence of an homologous series such as was here predicted, which contains more hydrogen than the benzole series and less hydrogen than the paraffine series. There is a great similarity between these Tertiary Russian petroleums and the California petroleums of the same geological age, and it is altogether probable that they both contain these "additive compounds of the benzole series". I am informed that during the last ten years or more there have been a number of thousands of barrels of petroleum refined in Santa Barbara and Ventura counties which has been sent into Arizona and Mexico, but was not of such a quality as to compete in the San Francisco market with oils manufactured on the Atlantic coast. On the whole, so far as I can learn, the oils manufactured from crude California petroleum are uniformly of inferior quality.

a S. F. Peckham, *Geo. Surv. of California:* Geology II, Appendix, page 73.

CHAPTER VI.—STATISTICS OF THE MANUFACTURE OF PETROLEUM DURING THE CENSUS YEAR.

SECTION I.—INTRODUCTION.

The statistics that form the subject of this chapter were obtained by means of a schedule of questions which were placed in the hands of the different manufacturers, and the answers have been consolidated into the totals as here given. Great care has been taken to include all parties engaged in the manufacture during the whole or any part of the census year, and it is believed that the list is complete. It is further believed that the schedules have been filled with as much care and regard to accuracy as could be expected under the circumstances. Several firms had gone out of the business at the time the statistics were compiled, and others had kept their books in such a manner as to render the compilation of such statistics difficult. It is believed, however, that in those instances where absolute accuracy was found to be impossible approximately correct estimates have been given. These instances constituted but a small percentage of the bulk of the business, which is carried on by large corporations and firms, who conduct their business systematically. The statistics furnished by these concerns have been compiled at much labor and expense, and in many instances are careful transcripts of annual or biennial balances and records kept in the regular course of conducting the business. As statistics of this character constitute a large proportion of the whole number, and as the remainder are carefully computed and estimated, the totals are believed to represent in a practically accurate manner the details of the business of the country for the census year.

The following-named firms and corporations have furnished statistics:

Name.	Location.
Portland Kerosene Oil Company	Portland, Maine.
Downer Kerosene Oil Company	Boston, Massachusetts, and Corry, Pennsylvania.
Oriental Oil Company	Do.
Maverick Oil Company	Do.
Pierce & Canterbury	Do.
S. Jenney & Sons	Boston, Massachusetts, and Brooklyn, New York.
G. F. Gregory	Do.
Charles Pratt & Co	Do.
Empire Refining Company	Do.
Sone & Flemming	Do.
James Donald & Co	Do.
Wilson & Anderson	Do.
Bush & Denslow	Do.
Franklin Oil Works	Do.
Devoe Manufacturing Company	Do.
McGoey & King	Do.
Queens County Oil Refining Company	Do.
James A. Bostwick	Brooklyn, New York.
Long Island Oil Works	Do.
Lombard, Ayres & Co	New York city.
Cheesboro' Manufacturing Company	Do.
Leonard & Ellis	Do.
A. C. Bunce & Co	Do.
Hudson River Oil Works	Bergen county, New Jersey.
Bayonne Refining Company	Bayonne, New Jersey.
Pennsylvania Refining Company	Philadelphia, Pennsylvania.
Malcom, Loyd & Co	Do.
William L. Elkins & Co	Do.
Harkness Refining Company	Do.
Webster Bros. & Wilson	Do.
Atlantic Refining Company	Do.
Excelsior Oil Company	Do.
United Oil Company	Baltimore, Maryland.
J. Parkhurst, jr., & Co	Do.
Camden Consolidated Oil Company	Baltimore, Maryland, and Parkersburg, West Virginia.
Solar Oil Company	Williamsport, Pennsylvania.
S. Bailey & Co	Danville, Pennsylvania.
Reading Oil Company	Reading, Pennsylvania.
Binghamton Oil Company	Binghamton, New York.
Vacuum Oil Company	Rochester, New York.
Buffalo Oil Works	Buffalo, New York.
Standard Oil Company	Cleveland, Ohio.
Pioneer Oil Company	Cleveland, Ohio.
Merriam & Morgan	Do.
L. D. Mix	Do.
American Lubricating Oil Company	Do.
Republic Refining Company	Do.
Backus Oil Company	Do.
William H. Doan	Do.
Schofield, Schurmer & Teagle	Do.
Forest City Varnish, Oil, and Naphtha Co	Do.
J. H. Heisel & Co	Do.
J. R. Timmins & Co	Do.
Acme Oil Company	Titusville, Pennsylvania.
Keystone Oil Company	Do.
White Star Oil Company	Do.
Crystal Oil Works	Miller's farm, Pennsylvania.
Imperial Refining Company	Oil City, Pennsylvania.
Mutual Refining Company	Reno, Pennsylvania.
Empire Oil Works	Do.
Eclipse Oil Company	Franklin, Pennsylvania.
Relief Oil Works	Do.
Franklin Oil Works	Do.
German Refining Company	Brady's Bend, Pennsylvania.
William Bradin	Millerstown, Pennsylvania.
Holdship & Irwine	Pittsburgh, Pennsylvania.
Standard Oil Company	Do.
Paine, Ablett & Co	Do.
E. J. Waring	Do.
A. D. Miller	Do.
J. A. McKee & Sons	Do.
Central Refining Company	Do.
D. P. Reighard	Do.
Andrew Lyons & Co	Do.
Wallover Oil Company	Smith's Ferry, Pennsylvania.
Samuel Hodkinson	Steubenville, Ohio.
Marietta Refining Company	Marietta, Ohio.
Ohio Oil Works	Do.
Argand Oil Company	Do.
Richard Patton	Do.
O. M. Lovell	Do.
Isaiah Warren & Co	Wheeling, West Virginia.
L. D. Crafts	Parkersburg, West Virginia.
Sweetzer Oil Company	Do.
S. P. Wells & Co	Do.
Chess, Carley & Co	Louisville, Kentucky.

SECTION 2.—CAPITAL, LABOR, AND WAGES.

The total amount of capital invested in the manufacture of petroleum during the census year was $27,325,746. Of this amount, $21,196,246 was employed the entire year and $6,129,500 for periods varying from one to eleven months, averaging $4,585,081 for twelve months. The total average amount of capital employed throughout the year was $25,781,327. (See page 183.)

The total number of hands employed was 12,231. The average number was: Men, 9,498; women, 25; children, 346; total, 9,869. Some of these men were employed in establishments that were in operation less than twelve months. The average number of men employed for twelve months was 8,032. Of the 9,498 men, 8,818 were employed by day and 680 by night. This latter number does not represent all of the labor employed at night, as in many establishments the work was not performed by men who worked constantly at night, but by men who were divided into sets and alternated, one set working during the day for one week, and at night the following week. In other establishments the work was divided from twelve at noon to twelve at night.

The wages paid for skilled labor varied from $1 50 to $3 per day, averaging about $2 25, and in general no difference was made in the wages of those who worked by day from those who worked at night. Ordinary laborers were paid from $1 25 to $2 per day, averaging about $1 50; coopers from $1 50 to $2 50, averaging about $2 25, and tinsmiths from $1 30 to $2 25, averaging about $2. The highest wages were paid on the Atlantic coast and the lowest on the Ohio river. The total amount paid in wages during the census year was $4,381,572.

SECTION 3.—MATERIALS EMPLOYED IN MANUFACTURING PETROLEUM.

The total amount of crude petroleum manufactured during the census year was 731,533,127 gallons, equal to 17,417,455 barrels of 42 gallons each. This crude oil was valued at $16,340,581, equal to 92.9 cents per barrel. During the year there was received by the manufacturers in—

	Gallons.
Barrels	20,363,918
Barges	42,433,388
Tank-cars	437,740,951
Pipe-lines	227,941,728

This oil is estimated to contain on an average 1 per cent. of water, and was mainly third-sand oil; but it includes also nearly all of the second-sand oil, and a portion of the first-sand. It does not include any of the heavy oils that are used as natural oil, and but a small portion, if any, of the mixed oils.

In the manufacture of this oil there was consumed the following kinds and amounts of fuel:

			Value.
Anthracite coal	tons	179,997	$446,922
Bituminous coal	tons	504,667	580,983
Wood	cords	1,471	6,355
Coke	bushels	303,596	13,218
Naphtha	gallons	2,892,164	42,315
Residuum	gallons	11,765,705	229,215
Total valuation of fuel used			1,319,008

Anthracite coal was very generally used in the Atlantic cities, but not to the exclusion of bituminous coal. Naphtha and residuum do not appear to have been used as fuel except in special cases. This fuel was used in the distillation of the oil and in the production of steam for use both as power and in distillation.

In the treatment of the distillates there were used of—

			Value.
Sulphur	tons	3	$180
Sulphuric acid	do	45,813½	1,206,052
Hydrochloric acid	pounds	3,424	68
Total value of acids			1,206,200

Of this vast quantity of sulphuric acid the "sludge" of 22,162½ tons was sold to fertilizer and chemical manufacturers, that of 21,158¾ tons was returned to the manufacturers to be restored, and that of 2,498⅛ tons ran to waste. Of this amount, 1,389 tons of the 2,498⅛ tons that ran to waste were thrown into the Atlantic ocean and rivers and bays that enter it, 839⅝ tons were thrown into the Ohio river and its tributaries, and 269½ tons into lake Erie. The proportion of sulphuric acid that is thrown to waste is now much less than it was formerly, but the nearly 5,000,000 pounds wasted during the census year is a large quantity with which to pollute our rivers and bays. The 1,678,000 pounds thrown into the tributaries of the Ohio river is a large contamination in the waters of even so large a river, and in addition to the acid the sludge oils cannot fail to increase its deleterious effects.

The alkali treatment was effected by means of—

			Value.
Soda-ash	tons	410.9	$10,427
Caustic soda	do	772.3	85,064
Sal-soda	pounds	96,643.0	1,423
Aqua ammonia	do	160,160.0	8,697
Lime	bushels	797.0	159
Total value of alkalies			105,770

The sludge of all of this alkali was run to waste on the Atlantic coast, into the Ohio and its tributaries, and into lake Erie.

The filtered oils and residues required the use of 1,990 tons of bone-black, valued at $62,815. The packages used were in part manufactured and in part purchased by the petroleum refiners, and were as follows:

		Value.
Barrels: Made	3,292,698	$4,040,502
Purchased	6,424,608	7,577,805
Total	9,717,306	11,618,307
Tin cans: Made	23,496,916	2,700,630
Purchased	344,173	93,367
Total	23,841,089	2,793,997
Packing cases: Made	1,607,297	189,511
Purchased	4,845,504	717,400
Total	6,452,801	906,911

The total number of all packages and their value was as follows:

Barrels	9,717,306	$11,618,307
Cans	23,841,089	2,793,997
Cases	6,452,801	906,911
Total packages	40,011,196	15,319,215

Where barrels are not made they are being continually repaired. The number of coopers employed was 2,062, and of tinsmiths, 353.

The following is the total cost of materials:

	Value.
Crude oil, 17,417,455 barrels	$16,340,581
Fuel	1,319,008
Acid	1,206,200
Alkali	105,770
Bone-black	62,815
Packages	15,319,215
Bungs, paint, hoops, glue, etc	645,412
Total	34,999,001

SECTION 4.—THE PRODUCTS OF MANUFACTURE.

There were manufactured of the volatile products of the distillation of petroleum of a specific gravity above 87° Baumé 293,423 gallons, valued at $29,117. This material was first called rhigolene, but a similar product has been called cymogene, and has been used in ice-machines. It is to be presumed that this material was used for that purpose. Of gasoline there was manufactured 289,555 barrels, valued at $1,128,166; of naphthas the following-named qualities and quantities:

Specific gravity.	Quantity in barrels.	Value.
Degrees.		
60	1,200	$3,600
62	109,472	225,609
63	18,945	43,039
65	6,148	17,339
68	7,300	20,075
70	918,374	1,188,201
71	1,617	4,657
71–72	6,899	18,110
72	6,048	3,931
73	38,777	45,945
74	19,565	54,110
75	8,100	34,425
76	11,609	39,315
68–70	12,525	16,282
65–70	260	780
60–72	42,302	109,417
68–78	3,400	8,500
65–76	85	60
Total	1,212,626	1,833,395

An inspection of the table on page 188 shows that the different grades of naphtha, as determined by the specific gravity, command very different prices. The following table shows the fire-test and quantities of illuminating oils manufactured:

Fire-test.	Quantity in barrels.	Value.
Deg. F.		
100	2,059	$6,435
110	6,083,026	19,035,913
112	613,979	2,621,777
115	90,814	313,560
120	2,107,220	7,096,218
110-120	5,948	16,844
130	510,522	1,507,884
135	2,036	11,233
140	15,000	85,000
150	1,170,725	5,494,833
110-150	28,270	108,557
155	1,960	7,350
160	1,627	9,040
175	22,843	164,914
150-175	46,220	350,144
Total	11,002,249	36,839,611

It will be noticed that the three grades of 110°, 120°, and 150° include the larger proportion of the illuminating oils. The specific gravity of these oils varies from 45° to 50° Baumé, the high-test oils having usually the highest specific gravity. But a comparatively small quantity of oils having a fire-test above 200° F. was produced.

Fire-test.	Barrels.	Value.
Deg. F.		
260	1,940	$8,245
285	300	3,000
300	14,304	191,480
Total	16,544	202,725

These oils are of a specific gravity of 36° to 39° Baumé.

The lubricating oils are prepared by various parties of different specific gravities. Petroleums reduced especially for cylinders are made very dense, and vary from 25° to 28° Baumé. Of these oils there were produced 26,018 barrels, valued at $371,020. Petroleums reduced for journals are prepared in greater variety. Of these there were:

Specific gravity.	Barrels.	Value.
Degrees.		
28	8,184	$30,327
28-30	105,095	506,957
29	63,705	306,203
29-34	26,657	179,510
33	1,200	7,020
Total	204,841	1,024,017

The distilled lubricating oils are in equally large variety. Of the deodorized lubricating oils there were produced:

Specific gravity.	Barrels.	Value.
Degrees.		
25	16,460	$148,140
26	2,017	9,580
28	68	340
29	12,440	149,280
28-33	39,430	304,232
Total	70,415	611,572

The paraffine oils reported are in still greater variety of specific gravity and price, ranging from about $2 to nearly $12 per barrel; the latter value being assigned to an exceptionally dense oil of specific gravity 20° Baumé. Of these oils there were produced:

Specific gravity.	Barrels.	Value.
Degrees.		
20	2,524	$24,230
20–27	8,733	33,297
24	552	4,068
25	26,293	165,555
26–28	6,000	45,000
27	3,187	6,055
28	31,462	124,077
33	714	5,141
Total....	79,465	408,023

Of paraffine wax there was produced 7,889,626 pounds, valued at $631,944, an average valuation of about 8 cents per pound, of which 900,000 pounds were made into candles by one firm.

Of residuum there was produced and sold 229,133 barrels, valued at $297,529.

The products of manufacture other than those already enumerated were chiefly petroleum ointment, harness oil, and other vacuum products, as follows:

The paraffine ointment manufactured had a value of more than	$100,000
Harness oil	34,513
Other products	193,584
	328,097

SUMMARY OF PRODUCTS OF THE MANUFACTURE OF PETROLEUM AND THEIR VALUE.

Article.	Barrels.	Value.
Rhigolene	5,868	$29,117
Gasoline	289,555	1,128,166
Naphtha	1,212,626	1,833,395
Illuminating oil	11,002,240	36,839,613
Mineral sperm	16,544	202,725
Reduced petroleum, for cylinders	26,018	371,020
Reduced petroleum, for journals	204,841	1,024,017
Deodorized lubricating oils	70,415	611,572
Paraffine oil	79,465	408,023
Residuum	229,133	297,529
	13,136,714	
Paraffine wax	* 7,889,626	631,944
Miscellaneous products		328,097
Total		43,705,218

* Pounds.

Section 5.—BUILDINGS, MACHINERY, ETC.

There were in use during the census year 374 boilers, of an aggregate capacity of 12,744 horse-power. The machinery was driven by 285 steam-engines, in addition to which there were 200 steam-pumps. These pumps were of very varied capacity and construction. Many of them were small, requiring only a few horse-power to run them, while others were very powerful machines, capable of handling hundreds of barrels of oil per hour. The number of buildings in use were reported at 866, and varied in character from rude sheds to substantial brick buildings, their aggregate value being $1,899,288, while the machinery was valued at $3,737,998. The losses reported as occasioned by fire and other accidents aggregate $104,631 43, a loss on the capital in use in the business during the year of four-tenths of 1 per cent.

An attempt was made to ascertain the quantities of the different products packed by the manufacturers for export, but a number of the returns contained so many errors that the results were worthless.

SUMMARY OF STATISTICS OF THE MANUFACTURE OF PETROLEUM DURING THE YEAR ENDING MAY 31, 1880.

Capital invested	a $27,325,746
Capital in use for twelve months	$25,779,688
Total number of hands employed	12,231
Average number of men employed	9,498
Average number of women employed	25
Average number of children employed	346
Total average number of hands employed	9,869
Total amount paid in wages	$4,381,572
Value of crude material	$34,999,001
Value of manufactured products	$43,705,218
Boilers in use	374
Horse-power of same	12,744
Engines in use	285
Pumps in use	200
Number of buildings	866
Value of buildings	$1,899,288
Value of machinery	3,737,998
Loss during the census year from fire, etc	104,631

STATISTICS OF PETROLEUM REFINING DURING THE YEAR ENDING MAY 31, 1880.

ESTABLISHMENTS:	
Number of firms and corporations	86
CAPITAL:	
Amount of capital invested	$27,325,746
HANDS EMPLOYED:	
Average number of men	9,498
Average number of women	25
Average number of children	346
Total	9,869
WAGES:	
Total amount paid	$4,381,572
MATERIALS:	

		Quantities.	Value.
Oil.			
Crude oil used (b)	gallons	731,533,127	$16,340,581
Fuel.			
Anthracite coal	tons	179,997	446,922
Bituminous coal	do	504,667	580,983
Wood	cords	1,471	6,355
Coke	bushels	303,596	13,218
Naphtha	gallons	2,892,164	42,315
Residuum	do	11,765,705	229,215
Chemicals.			
Sulphur	tons	3.0	180
Sulphuric acid	do	45,813.5	1,206,052
Hydrochloric acid	pounds	3,424.0	68
Soda-ash	tons	410.9	10,427
Caustic soda	do	772.3	85,064
Sal-soda	pounds	96,643.0	1,423
Aqua ammonia	do	160,160.0	8,697
Lime	bushels	797.0	159
Bone-black	tons	1,990.0	62,815

a This differs from the sum given in the Compendium ($27,395,746), an error of $70,000 having been detected after that was printed.
b The 731,533,127 gallons of crude oil used are equal to 17,417,455 barrels of 42 gallons each.

Packages.

	Quantities.	Value.
Barrels ....number..	9,717,306	$11,618,307
Tin cans ....do....	23,841,089	2,793,997
Cases ....do....	6,452,801	906,911
Bungs, paint, glue, etc		645,412
Total value of raw material		34,999,101
PRODUCTS:		
Rhigolene ....barrels..	5,868	$29,117
Gasoline ....do....	289,555	1,128,166
Naphtha ....do....	1,212,626	1,833,395
Illuminating oil ....do....	11,002,249	36,839,613
Mineral sperm........do....	16,544	202,725
Reduced petroleum, for cylinders........do....	26,018	371,020
Reduced petroleum, for journals ....do....	204,841	1,024,017
Deodorized lubricating oils ....do....	70,415	611,572
Paraffine oil........do....	79,465	408,023
Residuum........do....	229,133	297,529
Paraffine wax ....pounds..	7,889,626	631,944
Petroleum ointment, harness oil, etc........		328,097
Total value of manufactured products........		43,705,218
MISCELLANEOUS STATISTICS:		
Boilers in use		374
Horse-power of same........		12,744
Engines in use		385
Pumps in use		200
Number of buildings........		866
Value of same........		$1,899,288
Value of machinery........		3,737,998
Loss during the census year from fire and other accidents		104,631